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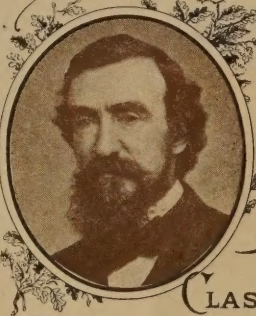
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THE CHEMISTRY AND PHYSICS OF CLAYS

AND OTHER CERAMIC MATERIALS

THE CHEMISTRY & PHYSICS OF CLAYS

AND OTHER CERAMIC MATERIALS

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PREFACE

The clay-working and allied industries are exceedingly old and have reached a remarkable state of perfection in craftsmanship, aided by only very little scientific knowledge. Within the last forty years, however, and especially during the last decade, increasingly stringent demands have been made by users of electrical and chemical pottery and refractory materials, and manufacturers of paper, textiles, and other materials in which clays are used, so that inherited and artistic skill is no longer sufficient, and Science must contribute to that knowledge of causes and effects on which future developments in these industries must depend.

Only those who have devoted special attention to the subject can be aware of the importance of the applications of both physics and chemistry to the industrial uses of clays and other ceramic materials. Such applications are so extensive, that it is remarkable that no volume has previously been published in which they are dealt with in a systematic manner, for there is scarcely a branch of physics or of inorganic chemistry which is not of value when applied to the treatment of clays, allied materials, and the products made from them, and the more intense such application, the greater is, and will continue to be, the benefit to all concerned.

It may well be asked why those engaged in such extensive and important industries as those connected with the manufacture or use of ceramic materials have paid comparatively little attention to the fundamental, scientific principles involved, and why so many advanced students of Science have largely neglected the study of clays and other ceramic materials ? The answer to such questions is threefold : (*a*) physicists have chiefly concerned themselves with the properties of matter in mass ; (*b*) students of pure chemistry, on the other hand, have chiefly dealt with the atoms and molecules of substances of a simpler character, the reactions of which can be more easily controlled, and whose properties and relationships can be studied in a more direct manner ; and (*c*) most manufacturers and users have scarcely realised, as yet, the enormous importance, to them, of chemists and physicists with a highly specialised knowledge of these materials.

The difficulties experienced in obtaining perfectly pure substances, the general insolubility and apparent inertness of most ceramic materials at temperatures below a dull-red heat, and the impossibility of obtaining many of them in some readily recognisable form—such as crystals of convenient size—have hindered research, but as these difficulties are overcome, and more and more information regarding the constitution and properties of these materials and products is obtained, great technical advances will be made.

The field of research in this subject is so vast, however, that it will be many years before it is fully occupied. At present, many important fundamental principles still need to be investigated, and far too little is known of what may appear to be such simple matters as the effect of the texture of many ceramic products, the causes and control of their strength, the distribution of the water in partially dried articles, and the relief of the various strains which are produced during the drying and burning of many pieces of pottery, or of other ceramic articles used in the construction of furnaces, coke-ovens, sanitary appliances, etc. The causes and

73804

prevention of distortion afford another wide field of investigation which has, as yet, scarcely been entered, and the complexity of the problems of chemical equilibrium in relation to ceramics is such that only the simplest cases are, as yet, reasonably well understood. Far too little attention has been paid to the enormous influence of the size of the particles on the progress and nature of chemical reactions, and of the physico-chemical changes which occur on heating clays and allied materials; and the study of such phenomena is, as yet, in its infancy. Colloidal phenomena also appear to offer almost endless opportunities for gaining further knowledge of the nature of clays and allied materials.

It will also be seen, in the following pages, that the chemical constitution of clays offers most fascinating problems, the complete solution of which has, so far, baffled the ablest chemists who have studied them, and a similar remark is equally applicable to increasing the plasticity of clays and to many of the other problems in physics and chemistry, with which those concerned with ceramic materials are in constant contact. Under these circumstances it will be obvious that the present volume is not intended to be an exhaustive treatment of the subject, but to provide, in a convenient form, such a description of the properties of various ceramic materials and articles, and of the application to them of the more important principles of chemistry and physics, as will be equally useful to students, manufacturers, and users. Several subjects of purely academic interest—such as the quantum theory and entropy—have been purposely omitted, as to have included them would have made the book unwieldy, without adding correspondingly to its usefulness.

Finally, the author wishes to acknowledge the zealous and skilled assistance of several members of his staff, without which this volume could not have been written. In this respect, he is specially grateful to Mr W. L. Emmerson, who has taken a large share in collecting data, made many useful suggestions and read the proofs, and to Mr F. Stones, who has assisted in other ways, including the compilation of the Index.

ALFRED B. SEARLE.

440 Glossop Road, Sheffield,
November, 1923.

CONTENTS

CHAPTER I.

PHYSICAL STRUCTURE.

PAGES

SOLIDS.—Crystalline substances—Crystallography—Multiple forms of crystals—Pseudomorphism—Amorphous substances—Glassy or vitreous substances—Colloidal gels—Cellular substances—Mixed materials 1–8

PASTES 8–10

SLIPS 10

COLLOIDS.—Colloidal state—Colloidal sols—Colloidal gels 10–13

STATES OF AGGREGATION.—Wholly crystalline—Granular—Granular fragments in a glassy matrix—Amorphous or crystalline fragments in a non-glassy matrix—Plastic materials—Amorphous or crystalline grains without cement 14–21

MASSIVE STRUCTURE.—Unstratified — Stratified — Foliated — Cellular — Capillary — Concretionary—Segregated—Fibrous 21–25

ALTERATION OF STRUCTURE.—Weathering—Grinding—Calcining 25–26

CHAPTER II.

PROPERTIES DEPENDING ON STRUCTURE.

TEXTURE.—Shape of grains—Size of grains—Grading—Materials producing a fine texture—Materials producing a coarse texture—Materials producing a medium texture—Texture of ceramic materials—Determination of texture—Comparison of different textures 27–59

HOMOGENEITY.—Treading—Wedging—Spade-mixing—Pugging—Tempering—Blunging . 59–61

POROSITY.—True porosity—Apparent porosity—Effect of texture on porosity—Materials increasing porosity—Materials reducing porosity—Effect of heat treatment on porosity—Effect of porosity on absorption—Effect of porosity on apparent density—Effect of porosity on spalling, etc.—Effect of porosity on thermal conductivity—Effect of porosity on resistance to corrosion—Effect of porosity on resistance to abrasion and erosion—Effect of porosity on electrical conductivity—Effect of porosity on strength—Effect of porosity on refractoriness—Effect of porosity on discoloration—Effect of porosity on the rate of drying—Porosity of ceramic materials—Determination of porosity and absorption—Penetrability 61–86

PERMEABILITY.—Effect of heat on permeability—Effect of permeability on thermal conductivity—Effect of permeability on drying—Permeability of ceramic materials—Determining permeability 86–93

CHAPTER III.

COLOUR, HARDNESS, AND MINOR PHYSICAL PROPERTIES.

COLOUR.—Natural sources of colour—Colours of raw clays—Colours of burned clays—Artificial colours—Colours of ceramic materials other than clay—Discoloration—Colour measurement. 94–123

HARDNESS.—Hardness of raw materials—Hardness of burned ceramic materials—Determination of hardness 123–137

MINOR PROPERTIES.—Ring—Feel—Odour—Sectility and Fissility—Friability . . . 137–138

CHAPTER IV.

STRENGTH AND ALLIED PROPERTIES.

PAGES

FORMS OF STRENGTH.—Cohesion—Tensile strength—Binding power—Brittleness—Friability—Malleability — Ductility — Extensibility — Elasticity — Flexibility — Toughness—Deformability—Crushing strength—Transverse strength 139–146

FACTORS AFFECTING STRENGTH.—Chemical composition—Size and shape of articles—Texture—Porosity—Power of bond—Mode of preparation—Grinding—Amount of water used—Proportions of added materials—Mixing—Ageing—Shaping—Drying—Burning—Repeated changes of temperature—Repeated heating—Temperature during use—Weathering—Frost—Blows—Deposited carbon—Corrosion by slags, flue-dust, etc. . 146–169

STRENGTH OF CLAYS AND CLAY PRODUCTS.—Raw clay and clay pastes—Dry clays—Burned clay wares 170–185

STRENGTH OF SILICEOUS REFRACTORY MATERIALS 185–188

STRENGTH OF OTHER REFRACTORY MATERIALS 189–192

STRENGTH OF GLAZES 192

DETERMINATION OF STRENGTH OF CERAMIC MATERIALS.—Tensile strength—Compression or crushing strength — Transverse tests — Impact tests — Torsion tests — Deformability tests—Freezing tests—Binding-power tests 193–202

CHAPTER V.

THE SPECIFIC GRAVITY AND DENSITY OF CERAMIC MATERIALS.

DENSITY.—Apparent density—Volume-weight—True specific gravity—Temperature—Mode of preparation and manufacture 203–205

FACTORS INFLUENCING APPARENT DENSITY.—Texture and porosity—True specific gravity—Temperature—Mode of preparation and of manufacture 205–207

FACTORS INFLUENCING APPARENT SPECIFIC GRAVITY 207–208

FACTORS INFLUENCING TRUE SPECIFIC GRAVITY.—Physical form—Chemical constitution—Impurities—Temperature of testing—Temperature and duration of previous heating . 208–212

APPARENT DENSITY AND TRUE SPECIFIC GRAVITY OF VARIOUS CERAMIC MATERIALS . 212–221

DETERMINATION OF SPECIFIC GRAVITY, APPARENT SPECIFIC GRAVITY, APPARENT DENSITY, AND VOLUME-WEIGHT.—Volume-weight—Apparent density—Apparent specific gravity—True specific gravity 221–226

CHAPTER VI.

CHANGES IN THE PHYSICAL STATE EFFECTED BY WATER.

PHYSICAL STATES OF CERAMIC MATERIALS 227–228

COLLOIDAL PHENOMENA.—Properties of colloidal sols—Electric charge—Electro-osmosis—Electrical conductivity—Electrical precipitation—Precipitation by electrolytes—Protection — Brownian movement — Osmotic pressure — Diffusivity — Specific gravity — Viscosity — Reversibility — Properties of colloidal gels — Absorption — Contraction — Action of heat—Adsorption 228–236

COLLOIDAL PROPERTIES OF CLAYS. — Hydrolysis — Hygroscopicity — Dehydration — Adsorption — Electrical properties — Brownian movement—Action of electrolytes—Flocculation — Deflocculation — Protection — Kataphoresis—Miscibility—Semi-permeability—Measuring colloidal matter 236–251

OTHER COLLOIDAL MATERIALS USED IN CERAMICS. — Active colloids — Alumina — Silica—Magnesia—Organic matter—Irreversible colloids 251–253

PAGES

PHYSICAL CHANGES EFFECTED BY WEATHERING.—Absorption of moisture—Distribution of moisture—Disintegration—Oxidation effects—Increase in plasticity—Artificial weathering—Influence of an excess of moisture in raw materials 253–257

SLAKING 257

PLASTICITY.—Nature of plasticity—Effect of size of grains—Effect of shape and structure of grains—Effect of aggregation of grains—Effect of surface area and intermolecular attraction—Effect of colloidal phenomena—Separation of colloidal matter from clays—Increase and reduction of plasticity—Proportion of water required—Effect of non-plastic materials—Effect of organic matter—Effect of adding colloidal matter—Increasing plasticity—Reducing plasticity—Plasticity and viscosity—Souring or ageing—Pseudo-plasticity—Oiliness—Mobility—Extensibility 257–276

MEASUREMENT OF PLASTICITY—Indirect methods—Direct methods 276–281

BINDING POWER.—Nature—Measurement 281–282

SLIPS AND SLURRIES.—Slips for engobes and glazes—Casting process—Purification of clay—Properties of slips—Measurement of viscosity 282–293

CHAPTER VII.

CHANGES IN THE PHYSICAL STATE FOLLOWING THE REMOVAL OF WATER.

DRYING.—Removal of water from slips—Removal of water from pastes—Dried pastes—Hygroscopicity 294–298

CHAPTER VIII.

CHEMICAL CONSTITUTION OF CERAMIC MATERIALS.

ELEMENTS.—Isotopes — Compounds — Mixtures — Solid solutions — Atoms and molecules—Atomic and molecular compounds—Laws of chemical combination—Law of multiple proportions—Atomic weight—Molecular weight—Valency 299–306

CHEMICAL NOTATION.—Formulæ—Structural or graphic formulæ—Molecular formulæ—Calculation of percentage composition from molecular formulæ—Calculation of molecular formulæ—Norms—Triaxial diagrams—Chemical equations 306–316

ACIDS, BASES, AND SALTS 316–322

MOLECULAR STRUCTURE OF SOLIDS.—Polymorphism 322–325

CHEMICAL CONSTITUTION OF SILICATES AND ALUMINO-SILICATES.—Silica—Silicic acids and silicates—Alumina and its hydroxides—Alumino-silicates—Raw clays—Burned or calcined clay—Synthesis of clay—Glazes 325–354

CHEMICAL CONSTITUTION OF OTHER CERAMIC MATERIALS. — Magnesia — Spinels — Silicon carbides and oxycarbides—Lime—Iron oxides and hydroxides—Chromite—Zirconia—Carbon 355–358

CHAPTER IX.

THE CHEMICAL COMPONENTS OF CERAMIC MATERIALS AND PRODUCTS.

CHEMICAL ANALYSIS.—Sampling 359–361

CHEMICAL COMPONENTS OF CLAYS AND CLAY PRODUCTS.—Interpretation of analyses—Impurities in clays—Silica—Alumina—Alkaline silicates and alumino silicates—Iron compounds—Calcium compounds—Barium compounds—Magnesium compounds—Titanium compounds—Manganese compounds—Phosphorus and Vanadium compounds—Sulphur—Moisture and colloidal water—Carbonaceous matter—Water of constitution and crystallisation 361–371

PAGES

Composition and Utility.—China clays—Ball and pottery clays—Fireclays—Brick clays—Fine earthenware—Coarse earthenware—China-ware and porcelain—Seger cones—Chemical composition and refractoriness 371–382

Chemical Composition of Engobes and Glazes.—Engobes or bodies—Glazes—Influence of constituents on engobes and glazes—Adjustment of composition—Typical glazes . 382–398

Chemical Composition of Other Ceramic Materials.—Silica bricks—Refractory silica sands—Silica glass—Spinels—Magnesite and magnesia bricks—Dolomite and dolomite bricks—Fused alumina—Zirconia, zircon, and zirconia bricks—Chromite and chrome bricks—Carbon bricks and crucibles—Carbides and carboxide bricks 398–405

CHAPTER X.

THE MINERALOGICAL COMPOSITION OF CERAMIC MATERIALS.

Microscopic Examination.—Rational analysis—Recalculated analysis 406–411

Mineralogical Composition of Clays.—Kaolinite and minerals similar to clay—Sillimanite and similar minerals—Impurities—Silica—Silicates, aluminates and alumino-silicates—Iron-bearing minerals—Calcium minerals—Barium minerals—Strontium minerals—Magnesium minerals—Aluminium minerals—Titanium minerals—Chromium minerals—Tin-bearing minerals—Manganese minerals—Phosphate minerals—Organic and carbonaceous matter—Water 411–423

Mineralogical Composition of Silica and Siliceous Materials.—Amorphous silica—Crystalline silica 423–426

Mineralogical Composition of Other Ceramic Materials.—Alumina and aluminous minerals—Magnesic minerals—Calcic minerals—Titanic minerals—Zirconium ores—Chrome ores—Carbon and carbon compounds 426–431

CHAPTER XI.

PHYSICO-CHEMICAL REACTIONS BETWEEN CERAMIC MATERIALS.

Avoidance of Chemical Action.—Chemical action and physical changes—Types of chemical action 432–437

Factors Influencing Chemical Reactions.—Heat — Time — Pressure — Vapour pressure—Surface tension—Viscosity—Solubility—Selective action—Catalytic action—Nascent action—Electrical conductivity—Light—Change of state—Intimacy of association—Relative quantities of reacting substances 437–449

Speed of Reaction 449–450

Reversible and Irreversible Reactions 450–452

Phase Conditions in Chemical Systems.—Phase rule—Equilibrium or phase diagrams—Solid solutions—Eutectics—Definite chemical compounds—Complex fusion curves—Time-temperature curves 452–466

Phase Conditions in Ceramic Processes—

Binary Systems. — Lime-silica — Soda-silica — Magnesia-silica — Barium oxide-silica — Strontia-silica — Zinc oxide-silica — Manganese oxide-silica — Iron oxide-silica — Zirconia-silica — Lime-alumina — Magnesia-alumina — Iron oxide-alumina — Iron oxide-lime — Silica-alumina — Silica-sillimanite — Iron oxide-magnesia.

Ternary Systems.—Lime-magnesia-silica — Lime-barium oxide-silica — Lime-lithia-silica — Lime-strontia-silica — Soda-lime-silica — Soda-lithia-silica — Soda-magnesia-silica — Soda-strontia-silica — Potash-lithia-silica — Barium oxide-soda-silica—Barium oxide-lithia-silica — Magnesia-lithia-silica — Lithia-strontia-silica — Iron oxide-magnesia-silica — Lime-alumina-silica — Potash-alumina-silica — Soda-alumina-silica — Barium oxide-alumina-silica — Magnesia-alumina-silica — Zinc-alumina-silica.

Quarternary and other systems 466–484

PAGES

Fusion.—Constitution of fused masses—Solidification of molten masses 484–489

Decomposition 490–491

Oxidation 491–492

Reduction 492–494

Corrosion.—Fireclay bricks—Silica bricks—Magnesia bricks—Bauxite bricks—Zirconia bricks—Carbon, chromite, and carboxide bricks—Measurement of corrosion . . 494–503

Chemical Reactions occurring at Lower Temperatures.—Action of water—Action of acids—Action of alkalies—Weathering 503–507

CHAPTER XII.

HEAT AND TEMPERATURE.

Heat.—Temperature 508–509

Heat Measurement.—Heat units—Calorimeters 509–510

Thermal Capacity.—Specific heat—Atomic heat—Molecular heat 510–514

Transmission of Heat.—Conduction—Thermal conductivity—Convection—Radiation . 514–519

General Effect of Heat on Substances.—Changes in temperature—Changes in volume—Changes in physical state—Changes in other physical properties—Changes in chemical composition—Electrical changes—Changes in optical properties 519–532

Temperature Measurement.—Temperature units—Temperature scales—Thermometers—Electrical pryometers—Optical pyrometers—Radiation pyrometers—Pyroscopes—Trials 532–542

CHAPTER XIII.

THE EFFECT OF HEAT ON CERAMIC MATERIALS.

Effects of Heat in Drying 543

Effects of Heat in Firing.—Smoking—Decomposition stage—Full-fire stage—Finishing stage—Vitrification—Finishing temperature 544–559

Effects of Withdrawing Heat.—Chemical changes in cooling—Physical changes in cooling 559–560

Effects of Excessive Heating.—Distortion—Boiling—Volatilisation 560–562

Effects of Prolonged Heating 562–563

Effect of Repeated Heating 563

Effect of Heat on the Volume of Ceramic Materials.—Permanent volume-changes—Reversible volume-changes 563–581

Effects of Sudden Changes in Temperature 581–584

Effects of Heat on Thermal Conductivity 584–594

Effect of Heat on Specific Heat of Ceramic Materials 594–599

Heats of Reaction in Ceramic Processes.—Heat of solution—Heat of formation—Heat of dissociation—Heat of transition—Latent heat of fusion 599–601

Effect of Heat on Refractoriness 601–607

CHAPTER XIV.

ELECTRICAL AND MAGNETIC PROPERTIES OF CERAMIC MATERIALS.

PAGES

ELECTRICAL CONDUCTIVITY AND RESISTIVITY OF CERAMIC MATERIALS.—Factors influencing electrical conductivity and resistivity—Electrical conductivity of clay—Porcelain—Silica bricks—Fused silica—Magnesia bricks—Zirconia bricks—Chromite bricks—Carborundum bricks—Clay slips—Determination of electrical conductivity, resistivity, etc. 608–620

MAGNETIC PROPERTIES OF CERAMIC MATERIALS 621

CHAPTER XV.

OPTICAL PROPERTIES OF CERAMIC MATERIALS.

IDENTIFICATION OF CERAMIC MATERIALS BY OPTICAL PROPERTIES. — Reflection — Refractive index — Double refraction — Polarised light — Optical sign — Optical activity—Pleochroism—Interference—Ultramicroscopic particles 622–631

OPTICAL PROPERTIES OF MANUFACTURED CERAMIC ARTICLES.—Transparency—Opacity—Translucency 631–634

LIST OF ILLUSTRATIONS

FIG.		PAGE
1.	Ungraded Mixture	32
2.	Mixture with Two Grades	32
3.	Mixture with Three Grades	32
4.	Schoene's Elutriator	51
5.	Lowry's Elutriator	53
6.	Boswell's Grading Graph	58
7.	Feret's Triangular Diagram	58
8.	Ludwig's Volumeter	84
9.	Seger's Volumeter	85
10.	Permeability Test	91
11.	Sokoloff's Permeability Apparatus	91
12.	Tensile Test-piece	193
13.	Tensile Testing Machine	194
14.	Vicat Needle	200
15.	Specific Gravity Bottle	225
16.	Viscosity Apparatus	291
17.	Rate of Drying	297
18.	Heating Curve of China Clay	349
19.	Fusion Curve of Felspar-Kaolin Mixture	365
20.	Fusion Curve of Mica-Kaolin Mixture	365
21.	Ludwig's Chart	382
22.	Phase Diagram of Water	455
23.	Albite-Anorthite Phase Diagram	457
24.	Phase Diagram of Wholly Miscible Liquids	457
25.	Phase Diagram of Miscible Liquids (with maximum point)	458
26.	Phase Diagram of Miscible Liquids (with minimum point)	458
27.	Phase Diagram of Miscible Liquids (with transition point)	459
28.	Eutectic Phase Diagram	460
29.	Solid Solution and Eutectic Phase Diagram	460
30.	Ternary Phase Diagram of Orthoclase-Albite-Anorthite System	463
31.	Ternary Phase Diagram of Quartz-Orthoclase-Plagioclase System	464
32.	Time-Temperature Curve	465
33.	Temperature-Composition and Time-Temperature Curves	465
34.	Phase Diagram of Lime-Silica System (Day and Shepherd)	467
35.	Phase Diagram of Magnesia-Silica System (Sosman)	469
36.	Phase Diagram of Lime-Alumina System (Sosman)	471
37.	Phase Diagram of Magnesia-Alumina System (Sosman)	472
38.	Fusion Curve of Alumina-Silica Mixtures (Seger)	473
39.	Phase Diagram of Alumina-Silica System (Sosman)	473
40.	Phase Diagram of Lime-Ferric Oxide System (Sosman)	475
41.	Triangular Diagram of Magnesia-Lime-Silica System (Ferguson and Merwin)	475
42.	Phase Diagram of Lime-Magnesia-Silica System (Wallace)	476
43.	Triangular Diagram of Lime-Alumina-Silica System (Little)	477
44.	Triangular Diagram of Soda-Alumina-Silica System (Wallace)	478
45.	Triangular Diagram of Magnesia-Alumina-Silica System (Sosman)	479
46.	Time-Temperature Curves of Crystals and Glass	489
47.	Thermo-couple Pyrometer	537
48.	Resistance Pyrometer	537
49.	Féry Radiation Pyrometer	539
50.	Seger Cones	540
51.	Refraction of Light	624
52.	Ultramicroscope	631

THE CHEMISTRY AND PHYSICS OF CLAYS
AND OTHER CERAMIC MATERIALS

CHAPTER I

PHYSICAL STRUCTURE

Clays and allied materials—conveniently termed *ceramic materials*—are so complex, both in their chemical constitution and in their physical structure, and some of their properties are so difficult to investigate that, in any attempt to study them, it is well to " begin at the beginning," and consider first the more obvious characteristics of their physical structure.

Like all forms of matter, ceramic materials, and the substances into which they can be decomposed, exist in one or more of three forms or phases, namely, *solid*, *liquid*, and *gaseous*, and in various transition phases such as (*a*) *pastes*, which consist of a mixture of solid and liquid phases, the former predominating; (*b*) *slips*, which are mixtures of solid and liquid phases, the liquid phase predominating; and (*c*) *colloids*, some of which are similar to pastes and others to slips, in each case the solid phase consisting essentially of particles of ultramicroscopic fineness.

Little is known of the gaseous phase of most ceramic materials, as the temperature required to convert them into this state is beyond the range of industrial furnaces.

Solids

Most people have a fairly clear idea of the meaning of the term " solid " as applied to any substance, though it should be observed that some apparently solid materials—especially certain glasses and under-cooled fused materials—are more correctly described as liquids which are so highly viscous as to present the appearance of solids. Speaking generally, however, solid substances are of a firm, compact nature, and each piece or portion of a solid has a definitely measurable length, breadth, and thickness, which are independent of the support on which the solid is placed. As is well known, ceramic materials occur in nature almost wholly in the solid state.

All solid substances may be divided into two important classes, namely, *crystalline* and *amorphous*.

CRYSTALLINE SUBSTANCES

Crystalline substances consist of units of definite geometrical form, or of fragments of such units, and in this way are readily distinguished, either by the naked eye or

by means of a microscope or other optical instrument, from amorphous substances, as the latter are not composed of such units.

Crystalline substances may occur in various forms according to their environment and mode of formation. The chief forms are :—

(*a*) **Perfect, regularly-defined Crystals.**—Such crystals occur in rocks which have cooled slowly from a molten state ; the least fusible minerals crystallise first and, unless their growth is impeded in some way, perfectly-shaped crystals are produced. Perfect crystals may also be produced when the liquid phase of a solution of one or more substances evaporates until the concentration of the liquid is too great for all the substances to remain in solution. If the rate of evaporation is rapid, small crystals will usually be formed, but if it is very slow—as is often the case in nature—very large and perfect crystals may be produced. Such crystallisation from solution occurs in nature in cavities in rock-formations, and it is also a result of metamorphism, in which case it is sometimes known as " recrystallisation."

Among many refractory materials which occur in the form of perfect crystals may be mentioned quartz, dolomite, various limestones and magnesite, very large crystals being sometimes found. Many artificial refractory materials, such as artificial corundum, sillimanite, carbides, and carboxides also form perfect crystals.

Crystals may occur either singly or associated in groups, when they are termed *twins*, *trins* or *triplets*, etc., according to their nature. Quartz, orthoclase felspar, and other minerals, frequently occur as twins, felspar having three distinct modes of twinning, whilst tridymite crystals, as their name signifies, consist of a union of three orthorhombic forms, which gives them a pseudo-hexagonal appearance.

Some crystalline substances are composed of a large number of simple " microliths," or of incipient and incompletely-formed crystals, which are termed " crystallites."

The use of ceramic materials in the form of coarse crystals is often very undesirable, as it sometimes renders the materials unsuitable, except after a costly treatment, such as calcining, grinding, etc. (see **Texture,** Chapter II).

(*b*) **Particles or aggregates of particles of irregular shape** and not exhibiting any outward appearance of being crystals, but which have an internal crystalline structure. This type of particle or grain is most common in refractory materials which occur as compact rocks such as quartzite, ganister, sandstone, magnesite, dolomite, limestone, etc. The irregular exterior and absence of crystalline form may be due—as in the case of rocks, such as rock-quartz, which have cooled from the molten state—to a large number of crystals being formed simultaneously and impeding the growth of each other, so that few, if any, were able to develop perfect crystalline outlines, the others taking the shape of the space in which they were crystallising and forming irregularly-shaped grains with internal crystalline characteristics. Such grains are, in fact, very similar to fragments of crystals, and resemble perfect crystals which have been subjected to a cutting or abrasive action, which has altered their external shape, but not their essential nature. The irregular crystalline grains in sedimentary rocks, such as sandstones, ganisters, etc., are composed of grains originally derived from igneous rocks, the constituents of which

crystallised irregularly as mentioned above. When an igneous rock is disintegrated, most of the loose grains are more or less irregular as a result of their mode of formation, and any perfect crystals which may have been present usually have their edges and corners removed by the attrition and corrosion which accompany prolonged exposure to weathering and other influences.

The fact that a mineral is crystalline in character, even though it may possess quite irregular external outlines, may be readily detected by examining it under a microscope with polarised light. With the exception of minerals of the cubic system —which are invisible in the dark field produced by crossed Nicol prisms—all crystals and fragments of crystals are equally visible in polarised light as in ordinary light, whilst non-crystalline (isotropic) substances are invisible, or almost invisible, under such conditions.

(*c*) **"Crystallites," "microliths,"** or **"incipient crystals,"** are generally formed by the agency of heat, and occur in nature in igneous rocks and also in some burned clay and other refractory products. They are not definitely crystalline, but possess a more or less regular shape. *Globulites* resemble small drops and are isotropic in character; *trichites* are hair-like forms, whilst *microliths* take the form of minute rods or needles aggregated into groups or masses of varied shapes. Augite, hornblende, felspars, etc., occur in rudimentary rocks in forms of this kind. Crystallites are usually colourless, but may, in certain cases, be black and opaque on account of a ferruginous coating.

Some minerals, especially quartz, frequently enclose grains of other minerals. This occurs when molten quartz crystallises around the other grains during the cooling of a rock from the molten state, or the quartz may have been deposited from solution around the mineral grains. Inclusions of this kind usually occur either in the centre of the crystal or as zones around the centre. The enclosed grains are usually termed *endomorphs*, whilst the enclosing minerals are designated *perimorphs*. The commonest inclusions in quartz crystals are rutile, hæmatite, limonite, pyrites, and chlorite. Calcite also frequently contains mineral inclusions.

Filaments or *streaks* (due to various causes) are frequently found in crystals; in orthoclase felspar, for example, they are a result of the partial kaolinisation of the material, whilst brownish *patches* and *blotches* may be due to decomposed magnetite. *Tufts* and *vermicules* of green ferruginous silicates and other minerals also occur in some clays.

Inclusions of pale-green or brownish glass, often containing immobile bubbles, sometimes occur in crystals of quartz, felspar, and other minerals.

In addition to solid inclusions, liquid and gaseous ones sometimes occupy cavities in crystals of quartz, felspar, etc. Cavities which are apparently empty or are filled with gas are usually spherical or elliptical in shape; sometimes they are so minute that a million of them could be contained in a volume of a cubic inch. Cavities filled with liquid and having sharply defined black borders when examined under the microscope are common in quartz crystals. They are generally spherical or elliptical, but are sometimes of a definite polygonal form; their size varies from microscopic dimensions to those sufficiently large to be readily visible to the unaided

eye. Such cavities contain water or salts of calcium, sodium, and potassium; they may also contain bubbles of gas—usually air or carbon dioxide. Cavities containing fluid are usually irregularly distributed, but they are sometimes confined to intersecting planes, as in some specimens of quartz, felspar, topaz, and other minerals.

Crystallography.—Substances which occur in crystalline form are characterised by one or more special forms, by which they may be identified.

Crystals are generally bounded by a number of flat or plane surfaces, though curved ones also occur, as in some dolomite crystals. When all the faces are similar in shape, the crystal is said to be of *simple form*, whilst if dissimilar faces occur, the crystal is a combination of two or more simple forms, and is termed a *combination*.

Unless distorted, all crystals have some form of symmetry, and crystals of the same mineral have the same type of symmetry. The shape of all normal crystals may be expressed in terms of lines or axes, which are the centres of planes which divide the crystals symmetrically in different directions. According to the form of the crystals these *crystallographic axes* may be equal or unequal in length, and either at right angles to each other or otherwise. Very careful examination has shown that six different arrangements of axes suffice to enable the shape of any crystal to be expressed in a simple manner, and as each of these arrangements of axes forms a definite " system," there are six systems of crystals. These are as follows :—

1. *The Cubic System.*—Crystals of this type have three equal axes at right angles, as *chromite*, *spinel*, *periclase*, and *magnetite*, all of which form octahedral crystals.

2. *The Tetragonal System.*—Crystals in this system have two equal lateral axes and one vertical axis at right angles. It is represented by *zircon*, *rutile*, and *anatase*, which usually occur as tetragonal prisms combined with tetragonal pyramids.

3. *The Hexagonal System.*—Crystals in this system have three lateral axes, making angles of 120° with each other, and a vertical axis perpendicular to the plane containing the lateral ones. In this system are quartz, which forms hexagonal prisms, together with positive and negative rhombohedra, the trigonal pyramid and trapezohedron and *calcite*, *dolomite*, *magnesite*, *corundum*, *hæmatite*, and *ilmenite*, which consist essentially of rhombohedra and scalenohedra.

4. *The Orthorhombic System.*—The crystals of this system have three unequal axes at right angles, and are represented by *andalusite*, which is a combination of the prism, basal plane, and sometimes a small macradome; *brookite*, which forms thin plates; *sillimanite*, which occurs as long needle-shaped crystals; and *tridymite*, which consists of three orthorhombic individuals and appears to be pseudo-hexagonal. The various varieties of *asbestos* also belong to the orthorhombic system and form long blade-like crystals, which give aggregates of crystals a fibrous structure.

5. *The Monoclinic System.*—The crystals of this system have three axes, one vertical, one lateral and perpendicular to the vertical axis, and the other at an angle to both. *Kaolinite*, *monazite*, *wolfram*, *scheelite*, *sphene*, *titanite*, as well as *orthoclase felspar*, *hornblende*, *mica*, etc., belong to this system.

6. *The Triclinic System.*—The crystals of this system have three unequal axes, none of which are at right angles, *e.g. cyanite*, *microcline*, and *plagioclase felspars*.

Multiple Forms of Crystals.—Although, under normal conditions, most sub-

stances crystallise in one definite form, this is not a necessary characteristic. For instance, crystals of widely-differing substances may possess identical crystal forms. Such minerals are said to be *isomorphous* (Gr. *isos*, equal; *morphe*, shape or form). Typical examples of this are calcite and magnesite, which both normally form trigonal crystals with a rhombohedral cleavage. These two minerals are able to replace each other in crystals of either material without any change in the crystalline form. Well-known crystals containing a mixture of these two minerals form the mineral *dolomite*. Other isomorphous substances are (i) alumina and ferric oxide; (ii) sodium and potassium oxides; and (iii) the plagioclase felspars. Thus, hæmatite will replace calcite, dolomite, quartz, barytes, pyrites, magnetite, rock salt, fluorspar, etc. Quartz will replace calcite, aragonite, siderite, gypsum, rock salt, hæmatite, etc.

Isomorphism is more fully dealt with in Chapter VIII.

The conditions under which crystallisation occurs may also be such that the same substance may crystallise in a different form. Substances which occur in crystalline form may have several geometrical shapes and are then said to be *dimorphous*, *trimorphous*, etc., according to the number of shapes they may assume when crystallising freely. These terms are not applied to crystals whose external forms are due to their being formed in unfavourable surroundings which hinder the development of the normal outlines of the crystals (p. 2). Calcium carbonate is a typical example of dimorphism, as it is capable of crystallising either in rhombohedral crystals, as in calcite, or in orthorhombic crystals, as in aragonite. Titanium oxide, which is known in three different crystalline forms (rutile, anatase, and brookite), is typically trimorphous. Where a substance has a still larger number of crystalline forms, it is termed *polymorphous*.

Pseudomorphism.—Some minerals have a crystalline structure which is not characteristic of them, and are then said to be *pseudomorphic*. Pseudomorphism may be due to (*a*) the secondary growth of one mineral around another, the former thus appearing to take the same crystalline form as the latter; (*b*) the infiltration of a solution into geometrical cavities left by the prior solution of other substances; the fresh solution crystallising and filling the cavity may take the same shape as the latter, and thus may appear to crystallise in the same form as the mineral which had previously occupied the cavity; (*c*) the gradual removal of portions of crystals by solution and a similar gradual deposition of other crystals from solution; and (*d*) the gradual change or metamorphism of a mineral by various agencies, so that in time the mineral has an entirely different composition, whilst still retaining its original crystalline form.

AMORPHOUS SUBSTANCES

Amorphous solid substances have no definite shape or geometric internal structure. They may be subdivided into (*a*) *glassy* or *vitreous* substances; (*b*) *colloidal* substances or *gels*; (*c*) substances of a *cellular* structure, such as kieselguhr, lava, etc.; and (*d*) substances which have no definitely recognisable structure and can only be described as amorphous. The term 'amorphous' is the converse of 'crystalline' and has reference only to the absence of a geometric internal structure, as many amorphous

substances have a definite, external form. For example, kieselguhr is seen, under a microscope, to have a perfectly-defined, cellular structure. The difference between amorphous and crystalline substances lies in the fact that whilst the latter, when crushed, still retain their definite structure, that of amorphous substances, being merely external, is destroyed when they are pulverised (see pp. 7, 8).

Glassy or Vitreous Substances.—Sometimes substances which have been cooled from a molten condition do not crystallise, but form isotropic, structureless, glassy masses. These glasses, even when containing few constituents, usually have a complex chemical constitution, and those formed naturally are often of bewildering complexity, because they have been produced by the fusion of a number of minerals into one homogeneous mass. Some of these glasses contain, as inclusions, irregular grains, crystals, or crystallites of other substances. The glasses may be of various colours, according to their chemical composition, though generally natural glasses are dark green in masses, but pale brown or nearly colourless in thin sections. Colourless, transparent glasses can only be produced in the absence of iron, copper, cobalt, and other compounds which form coloured silicates. Hence, colourless glasses are usually made of very pure lime, soda, or potash and silica.

In Nature, glassy substances occur chiefly in igneous and volcanic rocks, but they seldom occur to any serious extent in the raw materials used in the ceramic industries. In articles made from clay, on the contrary, a glassy or vitreous substance is a common constituent, and is, in fact, one of the most important substances produced during the firing of bricks, tiles, pottery, and other ceramic articles, the glassy material acting as a bond which unites the less fusible materials together and forms the whole into a strong, hard mass. Without this glassy material, the articles would be weak and fusible, and quite unsuitable for the purposes for which they are used. The nature and purpose of this glassy material in finished goods is more fully dealt with later, when considering the various types of structure in the raw materials and finished products.

The glassy material thus formed bears a closer resemblance to glazes and slags than to the glass of commerce and usually contains more constituents than the latter.

The *glazes* which produce a glossy appearance on pottery are also of the nature of glasses. The materials necessary for their production are finely ground, mixed in the required proportions, and then applied to the ware. The " glass " is then formed by heating the articles, so covered, in a kiln until the various constituents of the glaze react on each other and fuse to a viscous fluid which, when cooled at a suitable rate, produces a homogeneous glassy mass. Some glazes on clay-wares are partially crystalline ; this is largely due to the composition—the fluid at a comparatively low temperature not being able to retain some of the silicates in solution, with the result that they crystallise—but such crystallisation is also facilitated by very slow cooling. When a glaze, containing zinc or titanium oxides, is cooled slowly from 1300° C. to about 1100° C., some crystallisation usually occurs as the silicates of these metals are only slightly soluble. A " glass " which differs from nearly all others in containing only one constituent is made by fusing sand, or other fragments of quartz,

and is consequently known as *quartz glass*. It is a very valuable material for several purposes, as it is highly refractory and has an unusually low coefficient of expansion. In this respect it differs from most glasses which have a greater expansion coefficient and, consequently, are unduly sensitive to sudden changes in temperature, with the result that, when suddenly heated or cooled, they are very liable to break, on account of the internal strains which result from the irregularities in the expansion of the various parts of the material. Articles made of quartz glass, on the contrary, can be heated to redness and quenched in water without suffering any obvious ill-effects.

Some samples of quartz glass begin to crystallise or devitrify when heated for a long period between 1200° C. and 1600° C. Such a partially crystalline structure is undesirable, as ware in which it occurs is very brittle and is not so durable as when the material has a wholly vitreous or glassy structure.

Colloidal Gels.—Substances occur in clays and some allied materials which have been formed by the coagulation of colloidal sols, the coagulum being afterwards dehydrated and possibly hardened by pressure and other influences. Chalcedony and, possibly, flint and chert are of this character, but small proportions of other colloidal gels occur in many ceramic materials. Some of these colloids are quite permanent in character; others which are of a softer nature may sometimes be reconverted into the sol state by treatment with water containing a suitable salt such as sodium carbonate.

Colloidal substances are so important in connection with clays that they are more fully described on p. 10 and in Chapter VI.

Cellular substances are not common in clays; among other ceramic materials the most important ones with a cellular structure are: (*a*) those substances such as *pumice*, which are too fusible to be used to any great extent as refractory materials, and (*b*) *diatomaceous earths*, which consist of the minute, siliceous skeletons of dead marine and fresh-water plants such as *diatoms*, *radiolaria*, etc. One of the most extensively used refractory materials with a cellular structure is known as *kieselguhr*. Its texture is readily seen when it is observed through a microscope, though to the naked eye it appears to be structureless.

Moler consists chiefly of a similar material to kieselguhr, but it also contains a considerable proportion of clay and often of volcanic ash. The clay acts as a bond which unites the other particles into a fairly strong mass.

Other amorphous substances are those which have no definite crystalline form and cannot be included among the foregoing groups of amorphous materials; they usually occur as irregular granules, united to form larger masses or as stains or films on other grains. Dried or indurated clay is one of the commonest of such minerals; other amorphous clay-like substances are *halloysite*, *allophane*, *collyrite*, *nacrite*, and *lithomarge*.

Some forms of silica, such as *opal* and *siliceous sinter*, are amorphous, but may be colloidal gels (*supra*), whilst many crystalline minerals, such as *limestone*, *magnetite*, and *graphite* often occur in the amorphous state as a result of abnormalities in their mode of formation, or of the forces to which they have afterwards been subjected.

It is by no means easy to decide whether some substances are amorphous or

crystalline. If the particles of which they are composed are sufficiently small, their optical characters cannot readily be determined. The use of X-rays in this connection appears to be very promising (see Chapter VIII), and by this means W. H. Bragg has shown that china clay is largely crystalline in character, though the individual particles are far too small for this to be determined by other means. Many substances which appear to the naked eye to be amorphous are found, when examined by polarised light, under a microscope, to be crystalline. Thus, cryptocrystalline magnesite is sometimes termed " amorphous magnesite," but this is incorrect, as its texture is definitely crystalline, though the particles are extremely small. Hydromagnesite appears to be an amorphous variety of magnesite, but its ultimate structure has not been accurately determined.

Graphite, which is largely used as a refractory material, consists almost wholly of apparently amorphous grains. Doubt has, however, been expressed on the precise structure of graphite, and it may possibly be largely crystalline in character.

MIXED MATERIALS

Most ceramic materials are not homogeneous in structure, but consist chiefly of amorphous materials with a variable proportion of crystalline substances—usually present as impurities. Silica rocks, on the contrary, are largely crystalline in character and the amorphous material in them contains the chief impurities. Other refractory materials, such as magnesite, chromite, etc., may be either crystalline or amorphous, or a mixture. Artificially prepared refractory materials, such as carborundum, sillimanite, etc., usually contain both the crystalline and amorphous forms of the material.

Effect of Heat on Amorphous and Crystalline Materials.—The general effect of heat on crystalline materials containing combined water is to convert them into an amorphous form, this change being accompanied by some decomposition of the material. Most anhydrous crystals (apart from any decomposition which may occur) do not show any change until they fuse and form a viscous fluid, but some, such as quartz, undergo marked changes. Amorphous substances, when heated, usually tend to become denser prior to fusion. Most minerals which can be fused without decomposition will, if allowed to cool under suitable conditions, enter into the crystalline state.

The effect of heat on ceramic materials is by no means simple ; it is discussed more fully in Chapters VIII, XI, and XIII.

Pastes

Pastes are mixtures of one or more solids and liquids and, whilst they have many characteristics of both solid and liquid substances, are merely physical mixtures and not chemical combinations, yet they have additional properties which cannot be fully predicted from those of their constituents. Thus, a sample of brick dust may appear to have a physical character very similar to that of the dry clay from which it is made, but if each material is separately mixed with about one-fifth of

its weight of water, the clay will produce a paste which has very definite characteristics, such as its plasticity, flow under pressure, etc., which the wet brick dust does not possess. If the clay paste is allowed to stand on a slightly-sloping board it will harden gradually as a result of loss of water by evaporation, but the brick dust will allow a considerable proportion of water to drain away, and the solid material, as it dries, will become increasingly friable and will, at a slight touch, fall to powder. In other words, in a true paste, there is much more cohesion between the solid and liquid particles. This cohesion varies with different liquids ; thus, clay readily forms a paste with water, but not with paraffin or with alcohol.

The chief value of pastes in the clayworking and allied industries is the ease with which they can be moulded into convenient shapes, which they retain indefinitely.

Speaking generally, a satisfactory paste can only be produced when the solid constituent is in the form of a powder. Hence, indurated clays and massive pieces of material must usually be ground before they can be made into a paste.

Many clays occur in nature in a pasty form ; the consistency of such clays can be varied by adding more water, the amount required depending upon the nature of the material and on the amount of water previously present in it. The larger the proportion of water the more mobile will be the resultant paste.

Pastes may be regarded as very viscous fluids which require pressure to be applied to them before their " flow " can be observed. This property is due to the cohesion between the solid and liquid constituents, whereby the mixture forms a uniform mass in which the liquid acts as a lubricant facilitating the movement of the solid particles and simultaneously has a restraining influence and prevents them from being separated far from each other. The extent of this cohesion depends on the affinity between the particles of solid and liquid. It is high in *plastic* materials like clay, which have a high capacity for being deformed by pressure without separating the individual particles from each other, whilst materials in which the cohesion is low do not form good pastes and are termed non-plastic materials.

It was at one time thought that this cohesion or plasticity was due to the chemical constitution of substances which possess it, but it has since been ascertained that most insoluble substances, if sufficiently finely ground and partially converted into the colloidal gel state, become plastic. The practical difficulty—which is almost insuperable with most minerals other than clay—is to reduce them to such a fine state of division that plasticity becomes possible. Where no colloidal matter is present, the mixture does not form a true paste. Thus, a mixture of fine sand or rock dust and water does not contain sufficient colloidal material, so that the solid particles are held very loosely together, whereas a mixture of clay and water—which contains a considerable proportion of colloidal matter—forms a highly-plastic paste. The nature and effect of this colloidal matter are described more fully on p. 10, and in Chapter VI.

Pastes are employed in the manufacture of most articles produced in the ceramic industries. Thus, bricks are made either by introducing the paste into a mould and compressing it so as to fill the mould completely, or by extruding the paste through an opening of a suitable size, so that the paste issues in the form of a long

column which may be cut into pieces of the required length. Pastes made of refractory clays, etc., are used instead of mortar for laying bricks in furnaces, and for patching retorts, furnaces, etc.

Further information on pastes will be found in Chapter VI.

Slips

A *slip* or *slurry* is a mixture of solid and liquid in which the liquid predominates, so that the mixture may be regarded as a suspension of the solid matter in the liquid. The properties of clay slips are dependent chiefly upon the colloidal state of the suspended matter in them, but whereas the colloidal matter is in the *gel* state in clay pastes, it is in the *sol* state in clay slips. Slips may, however, be made entirely from non-plastic materials and water.

The properties of slips are also intermediate between those of solids and liquids, but a slip, like a liquid, takes the shape of the vessel into which it is placed. It also flows like a liquid and does not require any pressure to deform it, whilst a solid or a paste will not flow, but only changes its shape when subjected to pressure.

Slips are largely used in the manufacture of clay and other ceramic products by the process known as *casting*, in which the slip composed of the clay or other suitable material, mixed with water, is poured into a plaster mould of the desired shape. As the plaster is porous it absorbs some of the water and the interior of the mould is thereby covered with a thin coating of paste, its thickness depending on the time the slip remains in the mould. After a suitable interval any surplus slip is poured off and the mould is set aside to dry, after which it is easy to remove the solid material in the form of an article of the desired shape. The surfaces of some wares are also often coated with clay, clayey mixtures, or glaze, which is applied in the form of a slip, the ware being sufficiently porous to absorb the water and leave a thin coating of solid matter on the surface. The use of slips in this manner is often very convenient for applying cheaply and almost instantaneously a much thinner layer than would otherwise be practicable.

Further information on slips will be found in Chapter VI.

Colloids

A substance in the colloidal state is sometimes regarded as intermediate between that of a solid and a liquid, but, although many pastes and slips owe some of their properties to the colloids they contain, these colloids are something different from a mere mixture of solid and liquid. Thomas Graham, in 1861, discovered one of the chief characteristics of colloids when he found that certain liquids (apparently solutions of glue, gelatin, and similar substances) behaved quite differently from solutions of crystalline substances, inasmuch as the former would not pass through a membrane having water on the other side of it, whilst crystalline substances in solution passed readily through the membrane. To these non-permeating, amorphous materials he applied the term colloid (from *kolla*=glue or gum) and supposed that they were a separate class of substances. Since the time of Graham, however, it has

been found that most substances can be obtained in the colloidal state in the presence of a liquid in which they are insoluble.

The colloidal state may be defined as a physical condition of matter consisting of at least two parts [1] or phases, one (the *disperse phase*) being suspended or distributed in the other (the *dispersion medium*). The particles comprising the disperse phase are extremely minute, so that the force of gravity is counterbalanced by other forces which keep them in suspension. These forces are due to the electrical charge possessed by each particle, which causes it to repel other particles similarly charged, and, as the particles are closely associated, these repelling influences cause the particles to be in a state of constant unordered motion, visible under the microscope, which is termed the *Brownian movement.* This motion is only observable in liquids containing very minute particles in suspension, all the suspended particles having the same electric sign. If particles of opposite sign are introduced into such a liquid, the two groups of oppositely charged particles are rapidly attracted to each other and, as together they are too large to remain in suspension, they gradually settle to the bottom of the vessel and are said to form a coagulum. The coagulation or flocculation of a colloidal substance in this manner must not be confused with chemical precipitation, which is of quite a different character.

Colloids differ greatly from solutions, in that they have only a slight influence on the vapour-pressure, freezing-point, and boiling-point of the dispersion medium.

It was at first thought that colloidal particles were amorphous, and Graham proposed to distinguish them by using the terms *colloid* and *crystalloid*, but it has since been found that many crystalloid substances can be converted into the colloidal state whilst still retaining their crystalline structure. Thus, colloidal gold is almost certainly crystalline, and the X-ray spectrum of china clay recently obtained by W. H. Bragg suggests that what appears to be colloidal china clay is also crystalline; it is also very probable that other colloidal clays have a crystalline structure. As a general rule, however, most colloids are not crystalline, but resemble gelatin, milk, or the white of an egg.

Colloidal Sols.—The chief distinction between a "colloidal solution" and an ordinary suspension is that in the latter a settlement or deposition of the suspended particles occurs rapidly, whilst in a "colloidal solution" the particles remain indefinitely long in suspension as the result of a force which overcomes the natural tendency to settle as a result of the effect of gravitation. The maximum size of the suspended particles is limited by the effect of gravity; there is no known minimum limit to their size.

A suggestion by Wo. Ostwald, which has been largely adopted, is to regard particles greater than 0·0001 mm. as forming "coarse suspensions," those between 0·0001 and 0·000001 mm. as "colloidal solutions," and those smaller than 0·000001 mm. as forming molecular solutions. Colloidal sols are singularly sensitive to very minute quantities of certain substances, such as acids and salts, which cause the

[1] Whilst a solution is commonly regarded as a one-phase substance and a colloidal sol as a two-phase liquid, there appears to be a regular continuity between sols and solutions, so that this view must not be taken too rigidly.

particles to adhere to each other, or flocculate, forming larger masses which rapidly settle out of suspension and form a sediment.

Colloidal Gels.—When a colloidal sol is treated in such a manner that the suspended matter is coagulated, "flocculated," or so altered as to form a deposit or sediment, the product is often of a gummy or horny character and is now known as a *gel.* A gel appears to consist of an intensely fine network, the meshes of which can retain a very large proportion of water or other fluid. When a dry gel is placed in water it swells and becomes several times its original size. In its swollen state it is much more mobile and is almost a liquid. If the swelling can continue sufficiently, or if the mixture of swollen gel and water is well stirred, the gel may be broken up into a series of much smaller masses, which may form either a colloidal sol or a true solution according as the gel-forming substance is insoluble or soluble in water.

The chief colloidal systems which are important in connection with the properties of clays are : (*a*) particles of solid suspended in a liquid (solutions and suspensions) ; (*b*) particles of liquid suspended in a liquid (emulsions). In each case the material as a whole may appear to be solid, just as a jelly may appear solid and yet contain 95 per cent. of water. Plastic clays appear to be derived from colloids of the first group, whilst clay slips and slurries appear to be crude mixtures of colloidal sols and other substances. Other colloidal systems which are of some importance in connection with ceramic materials are : (*c*) particles of solid suspended in another solid in the form of a solid solution. This occurs in many minerals used in ceramics and also in many manufactured products, such as glazes, enamels, glasses, and the fused mass which binds the particles of many ceramic wares together ; (*d*) liquid particles suspended in a solid. Much of the liquid found in minerals is in this form ; (*e*) gas particles suspended in a solid, such as bubbles of gas suspended in minerals and in the finished articles produced in the manufacture of ceramic wares.

When the disperse medium is water the terms *hydrosol* and *hydrogel* are used. In the clay-working industries no disperse medium other than water is used, so that the terms *sol* and *gel* in this volume invariably refer to hydrosols and hydrogels.

Colloids may thus be divided into two classes : those consisting of a mobile liquid and referred to as *sols*, which are in turn divisible into *emulsoids*, in which both the disperse phase and the dispersion medium are liquids and *suspensoids*, in which the disperse phase is solid.

Colloids in the second class are termed gels ; they consist of a coagulated sol, and they have a cellular structure which, whilst clearly indicated by some of their properties, is too minute to be seen, even under a powerful microscope.

Table jellies are typical gels, but many substances, such as some clay pastes, are equally in the gel state.

Gels appear to be solid, but most of them, including those related to clays, contain a large proportion of water. Some organic gels contain as much as 95 per cent. of water and yet retain the appearance and many of the properties of a solid. By some means, which is not yet fully understood, the truly solid portion of a gel assumes a structure of a network or micellian character and can then absorb many times its weight of water without losing its characteristic properties as a solid.

If the dispersion medium (*e.g.* water) is evaporated, the gel hardens and in time may form a hard, horny mass, as in the case of chalcedony and glue. Where the treatment is not too drastic, a gel may be reconverted into a sol by a sufficiently powerful grinding mill, such as the Plauson mill, but when a gel has been dried drastically it is not always possible to reconvert it to the sol state. The chief characteristics of a dry colloidal gel are that, when mixed with water, it swells like glue, forming a soft mass or jelly, and when the latter is dried it shrinks and forms a dense, hard, and horny mass. When a sol is dried it is usually converted into a gel, but can often be reconverted into a sol by suitable treatment. In the case of clay gels, the simplest method is to stir the material vigorously with a very dilute solution of sodium carbonate, which will rapidly convert the greater part of the clay gel into the sol state.

The colloidal state of matter is of great value in the ceramic industries, as the binding of the solid particles together often depends largely upon the presence of colloidal matter. The plasticity of clays appears to be chiefly due to such material, and many non-plastic refractory materials which cannot be reduced to the colloidal state when merely mixed with water may be made plastic by the addition of colloidal matter. It appears to be quite certain that some of the most characteristic properties of clays are due to the fact that they contain colloidal matter, but it is scarcely correct to state, as some have done, that "clay is essentially a colloidal substance." A paste made of plastic clay appears to consist essentially of particles each of which is an inert, porous core, filled with and surrounded by a relatively large, yet actually very small film of jelly-like colloidal gel, which is able to retain sufficient water to enable the particles to move freely over each other when subjected to a comparatively light pressure, the particles retaining their shape when the pressure is removed. As such a mass dries, the jelly-like coating on each particle shrinks, drawing all the particles nearer together and forming an apparently non-colloidal, hard mass. Its plasticity and other characteristics may, however, be restored on mixing it with a suitable proportion of water. A material composed of minute spheres or "crumbs," each in turn consisting of a mass of interlaced lath- or plate-like insoluble crystals, could have many of the chief properties of clays, including plasticity, adsorption, shrinkage on drying, resistance to abrasion, and to various chemicals and semi-permeability. Hence, it is possible that plastic clays, contain a noteworthy proportion of matter of this nature, which would, under favourable conditions, show various colloidal phenomena. It is not necessary that the percentage by weight of colloidal matter should be large, as colloidal properties are all due to the nature of the surface of the particles.

The presence of matter in the colloidal state also explains the behaviour of many other substances used in the clayworking industries. Thus, when colloidal gels are heated, they change more rapidly than crystals of the same composition. This may account for the greater ease with which flint and other amorphous forms of silica may be converted by heat into other forms of silica far more quickly than silica in the crystalline state.

Further information on the colloidal state and its value are given in Chapter VI.

States of Aggregation

The various ways in which the components of ceramic materials are aggregated together is of great importance to the manufacturer, as it sometimes determines their usefulness.

The principal forms of aggregation or structure are :—

1. Crystalline.—The mass may consist wholly of crystals more or less perfectly developed and interlocking with each other to form a compact, impermeable material. Such structures are usually the result of slowly cooling a molten material, metamorphism, or crystallisation from solution (p. 2) ; typical examples are rock- and vein-quartz, quartzite, crystalline limestones, dolomite, and sometimes magnesite. Many artificial refractory materials, such as carbides and artificial alumina, are also wholly or partially crystalline.

The properties of a crystalline mass are in some ways advantageous and in others detrimental ; thus, when a material occurs in crystalline form it is generally fairly pure, although there is always the possibility of isomorphous replacement. Some crystalline materials have, however, the disadvantage of undergoing serious changes when heated, and this may cause difficulties when they are used. A typical example of this is quartz or quartzite, which is used in the manufacture of silica bricks.

When these bricks are heated, the silica is changed from the forms in which it usually occurs in nature to allotropic forms of lower specific gravity and, therefore, occupying greater space. This change occurs very slowly in the case of crystalline quartz, but much more rapidly when amorphous silica is heated. Thus, the cost of heat treatment is much greater for crystalline than for amorphous silica, and the conversion is not usually so complete. For this reason, a crystalline structure is not so desirable in the case of siliceous materials, but as the crystalline forms of silica are abundant and relatively pure, whilst the amorphous forms are more scarce and not nearly so pure, the crystalline forms are chiefly used.

Where the crystalline form is stable at high temperatures, it has the advantage that crystals are less easily attacked than amorphous material, and, therefore, bricks or other refractory articles with a suitable crystalline structure (such as sillimanite, tridymite, carborundum, corundum, periclase, etc.) are more refractory than those composed of amorphous material.

Where the material has an appreciable coefficient of expansion, crystals are more liable to crack and cause the disintegration of the ware than are amorphous grains. Wernicke has shown that quartzites of a wholly crystalline character (other than those consisting of tridymite) cannot be made into satisfactory silica bricks unless clay or other contractile bond is added to them. M'Dowell, on the contrary, has found that the most satisfactory quartzites used in America consist wholly of interlocking crystals. In general, such quartzites are not so satisfactory as those containing a siliceous cement.

From the point of view of users of refractory materials, satisfactory crystalline structures have almost negligible coefficients of expansion.

Wholly crystalline structures are fairly common amongst some raw refractory

materials, but are seldom seen in the finished products. In the latter, there is usually some other material between the crystals ; it is generally of a glassy nature. Wholly crystalline structures may be classified according to their coarseness into (*a*) *coarse crystalline*, in which the grains are readily visible to the unaided eye, and (*b*) *fine crystalline*, *micro-crystalline* or *crypto-crystalline*, in which the particles are much finer, the last two requiring a microscope to enable the crystalline structure to be identified. A fine crystalline texture is generally preferred both in raw and finished refractory materials, as it has some of the advantages of amorphous structures, without possessing in such marked degree the disadvantages of a coarse crystalline structure already enumerated. A moderately coarse crystalline structure is, however, desirable in the case of magnesite, as such materials are more readily calcined and the carbon-dioxide escapes more easily than from a fine-grained or crypto-crystalline magnesite. Crystalline quartzites in which the quartz grains show clear cracks are not suitable for the manufacture of bricks, as they tend to be weak along these lines.

2. Granular.—Most raw materials and finished products have a granular structure and consist of grains of either crystalline or amorphous matter cemented together by some form of bond which may be glassy, amorphous, or colloidal. In the raw materials, the principal cementing materials are quartz, opal, chalcedony, iron oxides (hæmatite, limonite, and magnetite), carbonates of calcium, barium, magnesium, and iron (calcite, witherite, dolomite, chalybite, and ankerite), sulphides of iron (chiefly pyrites), hydrated silicates (zeolites, chlorites, epidote, serpentine, talc), anhydrous silicates (felspar, hornblende, mica), sulphates of calcium and barium (gypsum, barytes), and various phosphates. Of these, the commonest cement is silica, but carbonates, sulphates, silicates, and iron oxides are also important cements.

Colloidal silica cement is usually produced by the weathering of silicate rocks ; the percolating waters containing the silica in solution descend until they reach a porous rock, in which the silica, being unstable, tends to separate from the solution and is deposited as a cement between the grains of the rock through which it is percolating. A siliceous cement may also be formed as a result of the silica being precipitated owing to an increase in the temperature of the solution. Many rocks are united by a calcareous cement derived from water containing carbon dioxide which has previously percolated through limestone or chalk and has dissolved some calcium carbonate. The solution is carried through the fissures and pores of other rocks until the carbonate is deposited and forms a calcareous cement.

Ferruginous cements are common in sandstones and other rocks ; they appear to have been formed by the percolation of water containing ferrous carbonate or hydroxide in solution.

Gypsum acts as a cement in some shales and sands. Thus, Fontainbleau sand contains sand-calcites which consist of isolated masses composed of gypsum and sand. Some of the Northumbrian fireclays are, according to Hutchings, cemented by barytes.

The precipitation of cements in rocks is usually a result of one of the following actions : (*a*) the mingling of solutions from different sources and their mutual

precipitation; (*b*) the chemical action between solutions and the rocks they traverse; (*c*) a decrease in temperature causing supersaturation; and (*d*) a decrease in pressure.

When the cement occurs in large proportions in a brickmaking or refractory material, it is generally undesirable unless it is very highly siliceous or argillaceous and is itself refractory.

In the finished goods, the cement produced by the burning process is usually of a very complex nature and is generally in the form of a homogeneous glass composed of various silicates, alumino-silicates, etc.

The larger particles or granules in a material of granular structure may vary greatly in size from that of pebbles (as in quartzitic conglomerates, which are sometimes employed for the manufacture of silica bricks) to the fine, amorphous grains which comprise the bulk of most clays, these latter being so minute as to render identification impossible, even when they are examined under a microscope. The granules may be either amorphous or crystalline or an indefinite mixture of materials in both these forms. The principal types of granular structure are as follows :—

(*a*) **Granular Fragments in a Glassy Matrix.**—These are not very common in raw refractory materials, though quite usual in igneous rocks. This structure is found in porcelain and in fired magnesia blocks or silica bricks, the two latter consisting of crystals of periclase and quartz and other forms of silica respectively, cemented together by a glassy mass composed of various complex silicates and alumino-silicates and sometimes including minerals such as wollastonite and anorthite, in which is embedded any crystals of tridymite and cristobalite which may be present. The whole mass is usually coloured by the iron compounds present in the raw materials. The granular matter may be either crystalline or amorphous and either coarse or fine.

Silica bricks may contain silica in any of the three allotropic forms of silica, so that the following structures may occur :—

(i) A mass of unaltered quartz grains united by a glassy bond.

(ii) A mass of unaltered quartz crystals and tridymite needles embedded in a mass of glass.

(iii) A mass composed wholly of tridymite and cristobalite united by a glassy matrix. This last texture is the most desirable, as such bricks are practically free from after-expansion and are very resistant to sudden changes in temperature.

Most commercial silica bricks are of the first type and contain only a very small proportion of tridymite and cristobalite. The best, however, should correspond to types (ii) and (iii) as the larger the proportion of tridymite and cristobalite in the articles after firing, the greater will be their value and durability. Silica bricks of type (i) are quite satisfactory if the grains are sufficiently small, but large grains make the bricks very sensitive to sudden changes of temperature, so that they tend to crack and spall when in use.

Some investigators, including O. Lange, Endall, and others, do not consider the presence of tridymite to afford any special advantage and have even stated that bricks rich in tridymite are weaker and more likely to crack than " unaltered calcined

quartz." They agree with others, however, that bricks made from erratic boulder or " Findlings " quartzite and some ganisters in which a contractile bond is present, are amongst the best and most durable when in use.

Ganister bricks consist of silica grains bonded together, partly with clay and partly with lime slurry. The resultant texture on burning is similar to that of ordinary silica bricks, but should preferably be of the type (ii.), p. 16.

Sand-lime bricks have a similar texture to ordinary silica bricks, the grains of quartz being cemented together by means of a complex lime-silica glass. The chief difference is that in a refractory silica brick each grain of silica must be small, whereas in a sand-lime brick the grains may be relatively large. The latter structure is not satisfactory for bricks which have to be repeatedly subjected to a high temperature, because they would then be liable to crack and be of very low durability on account of the strains set up when the large grains of quartz were heated (see p. 14). The prolonged heating to which silica is subjected when in use often effects a further conversion and an increase in the amount of tridymite or cristobalite crystals present. Thus, the siliceous hearths of acid-open-hearth steel furnaces, after being in use for a considerable time, consist largely of crystalline cristobalite at the surface with tridymite a little below it, both these materials being bonded by a glassy slag consisting chiefly of fayalite.

Sillimanite bricks should consist entirely of crystals of sillimanite, bonded by a small quantity of glassy matter, but, with the kilns at present available, this structure cannot be obtained unless the sillimanite is used as the raw material, together with sufficient clay to make the required bond. The ideal structure of glass pots, according to M. W. Travers, consists of a network of sillimanite crystals interwoven so as to form a strong and sufficiently dense mass. This is also the ideal structure of all refractory clay products, but it is never attained on account of the long period of heating which would be necessary to convert all the clay into sillimanite.

Bricks made of *artificial corundum* and, in some cases, those made of carbides, consist of crystals bonded together by a complex glass. The latter does not always fill all the spaces between the crystals, there being usually a number of cavities which render the material somewhat porous. Lime, carborundum, chromite, graphite, coke, and other refractory bricks consist of amorphous particles set in a glass composed of some fusible material which is mixed with the refractory material to give strength during the manufacture and to hold the particles together until they have been heated to a sufficiently high temperature to sinter and bind them into a hard, solid mass.

Bricks and other articles made of burned clay usually have a granular structure consisting of irregular grains of " burned clay," [1] united by a film of complex glass consisting chiefly of silicates and alumino-silicates. If the temperature has been sufficiently high, a few crystals of sillimanite, etc., may be formed, but these are unusual except in some porcelains and in fireclay articles of a highly refractory character, such as glass-melting pots. In most articles made of clay the proportion

[1] For the present this term is preferable to one purporting to give the constitution of the material.

of glassy bond or matrix is very small; it is larger in vitrified ware, such as paving bricks, some stoneware, and porcelain or china ware.

The texture of *clay-silica bricks*, or semi-silica bricks, is similar to that of other bricks, except that sand grains or crushed quartz rock are present along with the clay. Similarly, *grog bricks* are made of particles of burned clay (grog) as well as of raw clay.

Kieselguhr bricks consist of minute grains or cells of diatomaceous silica united by a glassy clay bond. On account of the nature of the kieselguhr (p. 7) the resultant bricks are extremely porous, this property being most important for this class of ware. Only just sufficient clay or other bond should be present to unite the particles together, any excess being useless and only tending to reduce the porosity of the finished articles.

Obsidianite bricks, such as those made by Charles Davidson & Co., Ltd., consist of grains of silica almost wholly enclosed in a glassy matrix, so that the material has a vitreous appearance and is quite impermeable. Such a material corresponds to an artificial porphyry.

(*b*) **Amorphous or Crystalline Fragments in a Non-Glassy Matrix.**—This structure is more frequent in the raw materials than in the finished products, as in the latter the strength of the articles depends almost wholly on the presence of some fused material to act as a bond. Many raw materials, however, consist of fragments which are cemented together by amorphous matter, which has been precipitated or otherwise deposited from solutions percolating through them. Thus, many sandstones consist of fragments of quartz cemented by amorphous iron, lime, barium, or similar soluble compounds, which have formed a film over the particles and produced a compact mass. The type of cement in a sandstone often gives the name to the stone. Thus, a siliceous sandstone is one which consists of grains of silica united by a siliceous cement. A calcareous stone has a bond consisting of calcium carbonate; a ferruginous sandstone, one composed of iron compounds, and so on. Sandstones with siliceous bonds are the only ones which can be used as refractory materials, as other bonds reduce the refractoriness of the stone to below the permissible limit.

The ideal structure of a quartzite for the manufacture of silica bricks is one in which the grains of quartz are very minute and are bound together with an amorphous cement. This is very important, as when a quartzite of this kind is heated the elastic nature of the cement reduces the expansion of the silica to a minimum, whereas a quartzite which does not contain any cement has a very marked expansion and frequently cracks on account of the strains set up in the material. One of the most suitable quartzites used for making silica bricks is the amorphous form found in erratic boulders and sometimes known as "Findling's quartzite." It consists of very minute grains of silica, surrounded by an amorphous siliceous cement, which is probably of a colloidal character (p. 7). Many other useful rocks are also characterised by a similar structure. The amorphous or possibly colloidal bond may be distinguished from the original quartz grains by examination with polarised light, though by ordinary light the rock appears to be crystalline. In some cases, silica

has been precipitated around irregular quartz grains and given the crystalline form of quartz. The Stiperstones quartzites near Shrewsbury are a good example of silicification, the sand grains having been enlarged by secondary growth, though crystal faces have not been produced. The ganisters of South Yorkshire and the Lickey quartzites are due to similar silicification, and many of the so-called *firestones* consist of an aggregate of irregular grains of quartz bonded by an amorphous or possibly colloidal cement composed of silica and sometimes of calcareous matter. Many shales and slates are often silicified by the deposition of silica in their fissures, and some limestones may also be cemented by what appears to be colloidal silica.

Laterites consist of amorphous mixtures of hydroxides of iron, aluminium, titanium, and manganese, iron hydroxide forming the principal bonding material. The bond is very weak in the freshly-obtained material, but on exposure its strength increases at the same time as the characteristic hardening of the material. Laterite may have been formed by the weathering of the basalts which lie beneath as in the Deccan of India, or from volcanic rocks, such as schists, gneiss, slate, sandstone, and granite, on which it lies, as in Africa. Holland has suggested that it may have been formed by the action of bacteria which precipitated silica in the colloidal form, the silica being removed by dilute alkaline solutions formed at the same time.

Bauxite has a structure very similar to laterite, viz. grains of an apparently amorphous material united by an apparently amorphous bond. Other refractory materials, such as some magnesites, also have a structure consisting of amorphous grains cemented by an amorphous cement. Thus, *crypto-crystalline magnesite* consists of minute grains of magnesite bonded with amorphous magnesium silicate, colloidal silica, or hydromagnesite.

Artificial products with a structure composed of granular pieces united with an amorphous yet not glassy cement are unusual in the industries with which the present volume is concerned. The most important are *carbon* or *coke bricks*, which consist of amorphous granules of coke or other form of carbon bonded together with an amorphous bond produced by the coking of the gas-tar or soft pitch with which the particles of coke were mixed.

(*c*) **Plastic materials** cannot be accurately described as united by any definite kind of cement, and yet in a dry state they are usually hard and granular, and so, from a structural point of view, they may be considered separately.

Plastic minerals—of which *clays* are the most important—consist largely of apparently amorphous grains, held together by extremely thin films of colloidal matter which surround each particle. In hard clays, this colloidal matter may be partially gelated, but on moistening with water it recovers its active properties and forms a plastic mass. It has long been considered by many investigators that china clay or kaolin consists chiefly of kaolinite crystals, but this was not definitely proved until recently, when W. H. Bragg obtained a characteristic X-ray spectrum. Unfortunately the flakes or grains of which the purest china clay is composed are so extremely minute that it is most difficult to accurately determine their shape. Some of them are aggregated together, forming fan-shaped masses termed *vermicules*; others have the appearance of a pile of coins, when they are termed *rouleaux*. Most investigators

accept the (unproved) suggestion of Aron, that the minutest grains of clay are spherical in shape. Whether china clay is composed wholly of kaolinite crystals, most of which are too small to be seen, yet remains to be proved, but there seems no reason to doubt its essentially crystalline nature. A few definite crystals of kaolinite occur in china clay, but the bulk of the material appears to consist of minute amorphous flakes. Scattered crystals of quartz and mica and small needle-like crystals of blue tourmaline also occur. In the cheaper qualities of china clay the proportion of these minerals may be high, but in the purified product they should only occur to a negligible extent. There are several apparently amorphous materials which are related to china clay. The most important of these are halloysite,[1] collyrite, allophane, nacrite, montmorillonite, and lithomarge.

Other clays also appear to consist chiefly of amorphous grains, but the particles are much too small for their shape to be recognised. When dry the particles appear to be amorphous and porous, but when wetted they become plastic and impervious to water. They behave as though permeated and surrounded by a colloidal jelly, which acts as a binding medium, though some investigators regard this as insufficient to explain their structure, especially when a clay has been heated to redness. The colloidal gel may thereby be destroyed or it may be converted into an amorphous cement, in which case burned clays should be included in groups (*a*) or (*b*) (see pp. 16 and 18), according to the temperature attained.

At present the structure of dry clays can only be described as "granular," that of wet clays as "plastic," that of slightly-baked clays as "granular, possibly with an amorphous cement," and that of fully-fired or vitrified clays as either "granular with a glassy cement," or as wholly vitreous or glassy. Further information will be found in the chapters dealing with the properties of clays dependent on their structure.

(*d*) **Amorphous or Crystalline Grains without Cement.**—Some ceramic materials occur in loose incoherent beds, without any cement to bind the grains together. Most sands, many decomposed quartzites and kieselguhr, are of this type.

Among the most important for refractory purposes is the Dinas sand—a pale-yellow material produced by the disintegration of the famous Dinas quartzite—occurring in the Vale of Neath, Glamorganshire. Several other refractory silica sands occur in various geological formations, especially in the Lower Greensand and Estuarine beds.

Dolomite sands are deposits caused by the weathering of dolomitic limestone; the calcareous material, being soluble in water containing carbon dioxide, is removed in solution, leaving the more magnesic material behind, together with more or less silica sand. Such sands are seldom pure enough for use as refractory materials.

Siliceous sinter sometimes occurs as loose sandy deposits, though it is often compacted, forming a fairly stratified mass. Chromite sometimes occurs as a loose detrital sand, the beds of which tend to be uncertain in extent. Zirconia and zircon also occur in the form of sands in river beds, etc., associated with other loose incoherent

[1] Ries considers halloysite to be always amorphous, the crystalline form being pholerite.

materials derived from pegmatites and syenites. Monazite sands are of a similar nature.

Many so-called " rare " refractory materials occur in individual grains disseminated through igneous rocks or in sand deposits and placers derived from the disintegration of such rocks. The principal of these are beryllium oxide, ceria, didymia, lanthana, thoria, yttria, etc.

Sands are usually produced by the disintegration of various rocks, either by such natural forces as wind and water, heat and cold, etc., acting on the surface or by various complex actions which take place in the interior of the rocks themselves, such as infiltrating water, hot liquids and gases from great depths, and other similar actions. Sands may be derived from all kinds of rocks, but those which are commercially valuable are generally derived directly from igneous or sedimentary rocks. The large class of siliceous sands used for furnace linings, etc., are generally derived from highly siliceous rocks, which may be either igneous or sedimentary. Loose detrital deposits may also be produced by precipitations from solution, as in the case of siliceous and calcareous sinters, etc., or by the deposition of the skeletons of dead organisms, as in the case of kieselguhr.

Massive Structure

The various components mentioned in the preceding pages may be combined in various ways, depending on the mode of formation, so as to form larger masses, the principal forms of which are as follows :—

Unstratified masses are those in which the materials show no special arrangement or lines of stratification. This type of structure is common amongst raw ceramic materials, and is also characteristic of many of the finished products. In fact, in the case of finished articles, it is the most desirable structure.

The nature of unstratified rocks comes within the province of geology, and is outside the scope of the present volume, though most primary clays, including china clay and some secondary ones, such as Boulder clay and the Pocket clays of Derbyshire, are unstratified, as are also some forms of silica rock, magnesite, and zirconia. Unstratified materials may be (i) homogeneous or uniform, or (ii) heterogeneous or irregular in character and in the arrangement of the particles of which they are composed.

Homogeneous structures are those which are uniform throughout the whole mass, and may, therefore, be expected to have the same physical properties, no matter from which part a sample may be taken. They differ from crystalline, stratified, laminated, and other heterogeneous structures in the absence of definite planes of cleavage, or other signs of being composed of " units " of different character.

In the manufacture of articles of ceramic materials, homogeneity is usually of great importance, and any definitely laminated or segregated type of structure must usually be destroyed during the process of manufacture.

As homogeneity is closely allied to " texture," further information on it will be found in Chapter II.

Stratified masses are those in which the materials are aggregated in the form of layers, strata, or laminations. This structure is characteristic of most of the rocks laid down by the action of water, and includes the majority of clays, most of which have been carried in suspension in water and have finally settled at the bottom of rivers, lakes, seas, etc., in beds or strata of varying thickness, often interlaid with strata of sand or other materials. For further details see the author's *British Clays, Shales, and Sands* (Griffin).

When a rock appears to be composed of very thin flakes, the material is said to be *laminated* and if the splitting occurs along the same plane as the bed in which it was deposited, the structure is termed *shaly*, but if the material cleaves in any other direction than one parallel to the bedding plane, the term *fissile* is employed to distinguish such a rock from the *shales*.

Many clays and all shales show signs of stratification; they may generally be split into thin flakes and foliations parallel to the bedding plane.

When the clay has been greatly compressed in a direction at a large angle to the bedding plane and simultaneously subjected to great heat, *slate* may be produced.

Flaky clays do not readily form a homogeneous plastic mass except after an excessive amount of grinding and are very difficult to use satisfactorily. The best clays have a perfectly homogeneous texture and are free from any laminated structure; but, for various reasons, laminated clays and shales are often used and with care can be made into satisfactory articles. It is, however, essential to break them down to such an extent as to destroy all the laminations, otherwise the various laminæ may not unite properly and the finished articles will be weak along the lines of cleavage.

Lamination in the finished goods may be due to (*a*) the use of unsuitable materials, or (*b*) the use of unsuitable methods of manufacture. It is prevented, where possible, by grinding or crushing the clay or other material so finely as to destroy all visible flakiness. This is not always practicable with plastic materials, some of which must be thoroughly dried before being ground. Where such drying is regarded as being too costly, soft laminated clays cannot be properly "tempered." The destruction of the laminations may sometimes be more easily effected if the clay is mixed with some non-plastic material such as sand. Some plastic clays—especially those of a "soapy" character—which are apparently free from laminations when first obtained, develop a laminated structure during the process of manufacture into bricks, etc. When this is the case, the method of manufacture is probably unsuitable, but the defect is sometimes avoided by adding non-plastic material prior to the tempering process. The production of *blisters* on the surface of articles is sometimes caused by the air between the laminations in the clay, especially when the articles are shaped by extrusion, through a die or mouthpiece. *Spalling* is also a result of lamination, though it may also occur as a result of internal strains, such as those produced when an article is subjected to sudden changes in temperature, and including those due to conversion of one mineral into another, as quartz into tridymite or cristobalite, or magnesia into periclase.

A form of lamination which is sometimes developed in articles which are repeatedly

heated and cooled, such as retorts and saggers, is due to the fireclay tending to re-crystallise in certain definite directions and so to develop lines of weakness. This defect cannot be wholly avoided, but may be diminished by carefully examining the broken saggers, etc., before re-using them, as pieces which have already developed this defect are naturally unsuitable. Glost saggers are particularly liable to cause this defect if they are crushed, mixed with raw clay and made into fresh saggers ; where possible, they should be avoided.

Lamination also occurs in some sandstones, ganister, bauxite, laterite, etc. Siliceous materials, other than clay, which show lamination should be avoided, as their structure is not easily destroyed in the course of manufacturing them into bricks, etc.

The best means of avoiding troubles due to laminations in clay products is to employ a suitable and thorough method of preparation of the clay. For some years there has been an increasing tendency to reduce the amount of treatment—especially in grinding, crushing, and tempering the clay—to a minimum and to omit weathering and " souring," with the result that ware made defective, as a result of lamination, is more common than formerly.

Sometimes a somewhat laminated structure is desirable, particularly in the case of graphite used for making crucibles. The best graphites for this purpose consist of small flakes, which adhere and form a laminated mass. Of American graphites, those from Alabama have the smallest and thinnest flakes, the flakes in Pennsylvanian graphites being slightly larger and thicker, whilst those in the Canadian graphites are still larger and more irregular. The graphite exported from Madagascar consists of grains nearly twice as large as those in the American graphites. Ceylon graphite is largely used ; it consists of very thin rectangular or triangular grains, rather than of true flakes ; it is very satisfactory and gives most durable products, whilst articles made from a coarser and more obviously laminated graphite tend to spall.

The excessively laminated structure of some graphites may be largely destroyed by mixing them with 15–20 per cent. of tar, briquetting the mixture, baking it quickly at 1000° C., and then crushing and screening the product so as to retain that between 18- and 100-mesh. This treatment is satisfactory for graphite for many purposes, but the product is not so satisfactory as natural Ceylon graphite.

Foliated structures are produced by the recrystallisation of some of the constituents of a rock along lines parallel to the original bedding or along joints or cleavage planes, the rock being afterwards subject to lateral pressure. A foliated structure is characteristic of the schists, but is not common in clays and other ceramic materials. Schistose quartz, on account of its foliated nature, is not satisfactory for making silica bricks, as those made from it tend to spall badly.

Cellular materials are not composed of a compact, dense mass, but are porous and apparently composed of " cells," as kieselguhr, moler, pumice, etc. A cellular structure may be produced by mixing combustible matter, such as sawdust, with the clay and other materials, so that when the articles are burned this combustible material burns out, leaving holes or pores in the space which it had previously occupied.

A preferable method of making articles of a cellular structure is to mix naturally cellular material, such as kieselguhr, with just sufficient clay to bind the particles together.

Capillary structure, *i.e.*, when a material behaves as though it were composed of a multitude of minute tubes, each having the diameter of a "hair," is somewhat analogous to cellular structure; it is characteristic of clays and many other ceramic materials. This structure is best understood by observing what happens when the lower end of a very narrow tube is dipped into a liquid which wets it; the liquid rises in the tube to a greater height than that of the external liquid, because the surface film of any liquid is under a tension equal to the surface energy per unit of area of the liquid. In the case of a vertical tube, the liquid creeping up it gains potential energy and equilibrium is established when this gain is equal to the loss due to the diminution of the air-glass surface. Thus, if the tube has a radius r, the total vertical force will be $2\pi r\mathrm{T}\cos a$, and this will equal the weight of the liquid raised, πr^2hdg.

Hence, $\mathrm{T}=\frac{1}{2}\,dgrh \sec a$ dynes per cm. But when the liquid wets the glass $a=0$ and $\sec a=1$, so that the surface tension $\mathrm{T}=\frac{1}{2}dgrh$ dynes per cm. when d is the specific gravity of the liquid, g the equation of gravity=981, r the radius of the tube, and h the height to which the liquid rises.

The capillary structure of china clay may be shown by several pretty experiments devised by Liesegang and Watanabe. Thus, if a solution of a coloured salt such as ferric chloride or ammonium bichromate be added to a clay slip, and the latter is then allowed to dry, forming a thin sheet or disc, the salt will not be distributed uniformly through the mass. A narrow band at the edge of the clay will be deeper in colour than the remainder of the mass, as the salt becomes more concentrated at the edge.

It has long been known that bricks and other porous substances, when saturated with a solution and then allowed to dry, segregate the greater part of the salt on their surface and form a "scum" or "wall white." Colloidal solutions behave in this respect in the same manner as true solutions. If to the centre of a dried disc of china clay containing ammonium bichromate a few drops of water are added, the water will drive the bichromate before it, so that there will be a central zone of water and around it a ring of deep yellow colour. If, instead of water, a few drops of silver nitrate are added in succession there will be a central red zone of silver chromate, around which is a ring of colourless silver nitrate which drives ammonium bichromate before it and forms a deep yellow or brown ring with an intervening colourless ring which is free from bichromate. Each additional drop, although placed in the centre, forms an additional ring. The appearance in this case is precisely the same as occurs in the well-known Liesegang rings, though the cause is quite different, as in the experiment with clay the periodicity of the rings is due to external causes, viz. the manner in which the drops are added, whilst in the jelly it is due to the structure of the system itself and is a phenomenon of diffusion. Diffusion rings may also be observed with clay, but they are so fine as to be almost invisible.

The rings obtained with solutions of (*a*) ferric chloride and potassium ferrocyanide, and (*b*) copper sulphate and potassium ferrocyanide respectively, on clay are

particularly beautiful and are wavy instead of plain. It might appear that semi-permeable membranes are first produced, but the rapid movement of the second drop shows that this is not the case. Apparently, a membrane formed in the presence of capillaries is not so closed as one formed by diffusion, so that the formation of rings is not uniform but irregular.

If, instead of applying the drops to the centre, the china clay disc is covered with a plate of glass and immersed in the second reagent, a different series of rings is formed, which, if the clay is saturated with copper sulphate and is immersed in a solution of soda, bear a close resemblance to malachite. These rings differ from the ones previously described in being the result of diffusion.

Concretionary structures consist of a nucleus surrounded with layers or aggregations of other materials, the whole forming irregular masses and nodules. This kind of structure is often formed from leaves, shells, or the remains of plants and animals deposited in water having salts or silica in solution. Limestones and various forms of silica occur in this form. Hæmatite, limonite, clay ironstone, and other forms of iron oxide commonly occur in concretionary masses. Oolitic limestones are frequently, and dolomitic sandstones more rarely, composed of concretionary masses. Flint occurs in nodular masses frequently of large size associated with calcareous matter. Bauxite and laterite often occur in small round grains, varying in size from a pea to 1 inch in diameter, the nodules being sometimes separated from the matrix. Crypto-crystalline magnesite also forms nodular accretions.

A concretionary structure is seldom produced in the course of manufacture of any clay products, as suitable conditions rarely occur.

Segregated structures are those in which part of the material forms veins or segregated masses in other rocks, such as vein-quartz, magnesite veins traversing masses of serpentine and hæmatite, spathic and magnetic iron ores occurring as large irregular masses in other rocks. Chromite frequently occurs in massive and lenticular forms and as veins traversing serpentine and peridotite rocks and also in irregular masses in residual clays associated with serpentine.

Fibrous structures in ceramic materials are rare ; the only one within the scope of this volume is asbestos, which is not really a refractory material, though it is sometimes used in the preparation of such articles as " fuel " for gas-fires and some asbestos bricks. It has a fibrous structure, the crystalline grains forming long flexible fibres which interlock and produce a strong mass. Of the several varieties of asbestos, chrysotile is specially valued on account of the strength and length of its fibres ; tremolite, crocidolite, and anthophyllite are of a similar nature, but their fibres are neither so long nor so strong.

Alteration of Structure

During the manufacture of articles of various shapes the structure of the original material is generally destroyed, so that a rock with an unsuitable structure may not be harmful.

The alteration of the structure of the raw material is effected in various ways,

such as (*a*) weathering, (*b*) grinding, and (*c*) calcining prior to making it into the desired shape.

Weathering consists in exposing the materials to the action of rain, snow, frost, etc., so as to break down the original structure of the clay or rock and render it easy to fashion into articles of various shapes. This method is commonly adopted in the case of soft, stratified materials such as clays, shales, etc. For harder and more resistant materials, which are not readily affected by the weather, this method is of little value and one of the other methods must usually be substituted.

Grinding is employed to break down compact masses into smaller grains. Granular materials bonded by amorphous matter, such as sandstones, clays, etc., are readily reduced to small grains, but with masses which are wholly crystalline or consist of crystals in a glassy matrix, the grinding may be a very difficult and expensive operation.

Wholly crystalline quartzites need to be ground so fine before their structure is destroyed that the cost is often prohibitive, so that it is usually preferable to use a slightly less pure material which can be more easily reduced to a suitable state.

Materials of a shaly character sometimes cause difficulty by producing flat plates or flakes, which are very undesirable in the finished goods.

Calcining consists in heating a material to redness or to a higher temperature, usually in order to partially decompose it. Such treatment is often useful in altering the structure of limestone, dolomite, magnesite, clay, flint, and some quartzites, sandstones, etc. In some cases, such as the first four substances just mentioned, the change in structure occurs as a result of chemical dissociation, whilst in the last two substances various changes in volume occur, with the result that strains are set up in the material, which cracks and can then be readily reduced by crushing to a structureless sand.

CHAPTER II

PROPERTIES DEPENDING ON STRUCTURE

Some of the properties of ceramic materials are directly dependent on their structure. The principal of these are: (*a*) texture, (*b*) homogeneity, (*c*) porosity, and (*d*) permeability.

Texture

The texture of a material is concerned with (*a*) the shape of the individual grains comprising its mass, (*b*) the sizes of the various grains, and (*c*) the grading of the grains, *i.e.* the proportions of particles of various sizes.

The texture is said to be *coarse* when the particles are large or loosely spaced, and *fine* when the particles are small. Sometimes a material with a cellular structure (p. 23) is regarded as having a coarse texture. When it is difficult to observe the texture with the naked eye a pocket lens or low-power microscope may be used, and in some cases it is easier to examine the texture if the material is first ground smooth and then polished.

The texture of a material has a very important influence on many of its properties, including shrinkage, porosity, fusibility, and, in the case of clays, plasticity. Notwithstanding its importance, it is not considered or controlled to anything like the extent it should be, and many failures in the production and use of articles from clay and other ceramic materials are due to the lack of proper attention to this property.

The shapes of the grains of a material should be such as to ensure: (*a*) the maximum strength; (*b*) the requisite porosity and permeability; and (*c*) a surface of the desired smoothness. The grains of the materials under consideration may be (*a*) flat or flaky, (*b*) angular, or (*c*) rounded.

Flat or flaky particles are usually undesirable, as they tend to cause lamination troubles (p. 22), so that materials which have a flaky texture, such as mica, should generally be treated in some way (such as grinding, calcining, etc.), which will either destroy the flakes or remove them, otherwise the material should be discarded except in the case of graphite used for crucibles (p. 23), and even then the flakes must be sufficiently small. Large flakes in any kind of ware are undesirable, as they tend to produce lamination.

Angular and rounded grains are conveniently considered together rather than separately. Rounded grains which are perfect spheres and all of the same size,

produce a mass of maximum porosity if the grains are piled vertically on one another. The porosity is slightly lower if one grain out of each four rests equally on three others, yet is still higher than with angular grains. This is due to the fact that rounded grains of one size will roll together easily, but, on account of their shape, they cannot interlock, so that it is impossible for the interstices between the particles to be filled. When rounded grains of various sizes are present, the amount of interstices is less, though still larger than with angular grains which interlock to some extent, and may, therefore, fill some of the interstices by projecting portions of the grains. A strict comparison in simple terms is impossible, because rounded grains readily roll over one another until a state of minimum porosity for such grains is attained; but angular grains require a certain amount of pressure and shaking before they will arrange themselves in a position of minimum porosity, and if this is not applied their irregularity and imperfect interlocking may cause them to produce a more porous mass than one in which rounded grains are used. No matter how much pressure, short of crushing them, is applied to rounded grains, they will always produce a porous mass, as the interstices cannot be filled. Such pressure is transmitted equally from grain to grain and a mass of uniform porosity is produced. When a state is reached in which every particle is resting on three others, the minimum attainable porosity is reached and no matter what further pressure (short of crushing) is applied, the porosity will remain constant.

With angular grains, on the contrary, the conditions are different, an increase in the pressure causing the particles to interlock more closely and so reduce the porosity of the mass, the interlocking being dependent, to a large extent, on the pressure applied. Moreover, the pressure is not transmitted uniformly through the mass, as when rounded grains are employed, but is greatest nearest to its source and least at the greatest distance from it. Consequently, the porosity varies in various parts of the mass and, unless there is sufficient water present, a non-homogeneous article is produced with a great tendency to spalling when it is subjected to sudden changes in temperature. Hence, when it is desired to produce the most uniform mass, rounded grains are preferable to angular ones. Round grains also give a more permeable mass on account of the smaller fractional resistance to the passage of gases and liquids. Angular grains, on the other hand, have an effect equivalent to a rougher surface and offer a greater resistance to the passage of gas and liquids through them.

As rounded grains do not interlock, the resulting mass is very weak, friable, and incoherent, and unless restrained by the vessel in which they are contained, the particles roll over one another and shear when pressure is applied to them. Angular grains, on the contrary, readily interlock and form a strong, compact mass and are, therefore, preferable when great strength is desired.

Materials composed of angular grains require a larger proportion of binding material to produce a compact mass than those composed of rounded grains, on account of the greater surface area of the angular grains. They have the advantage, however, of presenting a larger surface to the action of the bond and so produce a stronger mass.

From the above comparisons it will be seen that the shape of the particles must be varied according to the particular properties required. Thus, rounded grains are undesirable in the banks of open-hearth furnaces, as they cannot be placed so as to form a steeply-sloping bank, their angle of rest being very low. For this purpose angular grains are preferable, but they should not be too angular, or they will not give a mass of sufficient compactness unless tightly rammed into position. For such a purpose the best material is intermediate between angular and rounded grains, namely, sub-angular ones, though highly angular grains are often preferred in the copper furnaces of South Wales and in America, where crushed quartzite is used. The facing sands used for casting should be made of sharp angular grains, as a strong mass is required to resist the cutting action of the molten metal when it comes into contact with the sand. The sands used for " backing," however, consist of rounded grains, as in them strength is less important than permeability. In some cases, rounded facing sands are used so as to secure ample permeability, but it is always at the expense of the strength.

For making articles which are required to have a certain amount of strength, angular grains are generally required, even though some other properties must be sacrificed. Thus, ganister is specially valuable on account of the irregular splinters which it forms when ground, interlocking readily and forming a dense and compact mass. The process of grinding any material always tends to produce rounded grains. Hence, if angular grains are required, the material should be crushed with hammer-like blows, as distinct from the rubbing action of most grinding machines. For the same reason, when preparing " grog " it is best, if possible, to burn the clay in lumps rather than to grind it and make it into rough clots. The calcined clay or grog may afterwards be crushed without undue rounding of the grains.

Sometimes, during the burning of ware, long, lath-like crystals are formed, which produce a very strong mass on account of the interlocking which occurs. Thus, an ideally fired clay, such as that largely attained in refractory porcelain, consists largely of a mass of interlocking crystals embedded in a glassy mass ; the crystals give it great strength. Needle-shaped crystals are especially valuable for producing a strong mass, as they interlock more completely than relatively shorter and thicker ones.

In the manufacture of bricks, pottery, etc., the shape of the particles is very important, especially if they are large, as the latter, if rounded, are more likely to cause trouble. The determination of the shape of the grains of any particular material is best effected by examining the material with a pocket lens, or, if necessary, with a microscope, as described in Chapter X.

The possibility of producing grains of a suitable shape depends chiefly on the nature of the material, some substances being quite unsuitable. Stamps, disintegrators, crushing rolls, and edge-runner mills with perforated pans usually produce angular particles, whilst ball-mills, tube-mills, and edge-runner mills with solid pans generally form rounded grains. With some materials, crushing rolls tend to form flaky particles.

The sizes of the grains in both raw and fired ceramic materials vary greatly

according to the purposes for which the materials or articles are to be used. Instead of the terms "large" and "small" grains, it is more usual to refer to them as "coarse" and "fine."

Coarse grains usually produce a less porous mass than one composed of fine grains, but the average size of the pores is larger in the coarser-grained material, so that its permeability is greater. In the case of fired ware, the fine grains are less refractory than the coarser ones, and if they partially fuse when heated they will produce a less porous mass on account of the closing up of some of the pores with glassy matter. For this reason, whilst an unfired, fine-grained mass may be more porous than a coarse-grained one, the former, after it has been heated, may become much less porous. Hence, in ware fired at a high temperature, coarse grains must be used where a great porosity is required, because such pores are not so readily filled by fused matter as when a fine-grained material is used.

Coarse grains are also desirable where the maximum permeability is required, as this property depends on the size of the pores as well as on the total amount of pore-space (see *Permeability*).

Coarse particles are preferable in most cases where resistance towards sudden changes in temperature is required in any materials which have an appreciable coefficient of expansion, because, in a close-grained mass, the strains due to the heating or cooling cannot be relieved by the rearrangement of the particles without the disruption of the mass. When the change in temperature is not too rapid, many close-textured firebricks are very durable under adverse conditions if they are made of properly-graded material. As most of the materials described in this volume have a low thermal conductivity, the coarser grains do not attain the temperature of the furnace so rapidly as the smaller ones, so that the former are able to stand much higher temperatures than the latter (see also Chapter XIII).

Substances which undergo only a very small change in volume when heated or cooled may be composed of either small or large particles so far as their resistance to changes in temperature is concerned. All argillaceous, siliceous, bauxitic, magnesic, dolomitic, and similar materials have an appreciable coefficient of expansion, and this must be allowed for in considering the size of particles to be used where great or sudden temperature changes are to be withstood (see also Chapter XIII).

The presence of large grains reduces the strength of materials containing them, both in the unfired and fired states, as the strength depends on the area of contact between the various particles, *i.e.* on the compactness of the mass. Coarse grains are less readily attacked by corrosive substances than fine grains, as they have a smaller surface area for the same mass. For the same reason they require a smaller proportion of bonding material and of water to make a paste of the required consistency. Consequently, a shorter time is required for drying and the shrinkage will be less. On the other hand, though small grains require more water, they are more easily moulded to the required shape.

Coarse grains usually produce a mass of more open texture, so that corrosive substances are more able to penetrate into the interior of the mass and so reach a greater surface upon which they may act than is the case with a mass composed of

smaller particles, which do not allow the corrosive agents to penetrate so far into the interior. Hence, whilst fine-grained materials are superficially attacked more rapidly, they are often preferable for resisting corrosive influences on account of the impermeable surface they rapidly form.

Where a change of crystalline form is required, as in the case of quartz in silica bricks, it is often desirable to use fine particles which will be readily converted. When a fusible material is required, as in the production of glazes, glass, and fused quartz, the finer the particles the more rapidly will the fusion be effected.

Where chemical reactions are required, the size of the grains influences the speed at which they react; fine grains react more rapidly than larger grains because they have a large surface area and, being smaller, they have a wider field of action. This subject is more fully dealt with in Chapter XI.

Materials composed of coarse grains have a rougher surface than those made of smaller grains. In some cases the roughness is not serious, but where corrosive substances are present as smooth a surface as possible is desirable.

Fine-grained materials, when wetted, sometimes have the serious disadvantage of entrapping air between the grains, thus causing a form of lamination (p. 22) which creates defects in the finished articles.

Grading.—Besides the sizes of the individual grains it is also most important to consider the grading of the material as a whole, because in only a limited number of cases can a material consisting of particles of only one size be used satisfactorily. Thus, a material in which all the grains are uniform in size is undesirable for bricks and similar articles, as such grains, even when angular, do not bind well together. A much stronger and better product is obtained if the particles are of different sizes, so that they may interlock properly and, aided by a natural or added bond, may produce a material having the properties which it is desired it should possess.

The term *graded* is applied to any material composed of grains of various sizes, the proportion of grains of each size being such that the mixture has certain properties, such as high strength, low permeability, etc. It is sometimes misapplied to heterogeneous materials, in which the proportions of particles of various sizes are quite accidental, whereas in a properly graded material they are present in just those amounts which are the most suitable for a particular purpose. Some materials have been graded naturally by the manner in which they were deposited, but others must be subjected to a screening or other mechanical process which will remove particles of undesirable sizes. Alternatively, a graded material may be produced by mixing grains of selected sizes in suitable proportions, though such artificial mixtures are seldom as homogeneous as the natural graded materials.

The use of graded material is desirable for several reasons :—

(*a*) If only coarse material were employed, it would require a very large proportion of bond to fill the voids and cement the grains together, and the resultant mass could not be so strong as a better-graded material, on account of the small number of points of contact between the " cement " and the larger particles.

(*b*) The porosity and permeability are reduced in a properly graded material, and this often has a marked effect on its resistance to corrosion, abrasion, etc.

(*c*) The appearance and other good qualities of a material may often be improved by removing particles of certain sizes from the remainder, as when pebbles are washed or screened out of a clay or sand.

(*d*) The use of carefully-graded material greatly lessens the possibility of spalling, splintering, and cracking when a material or article is exposed to sudden changes in temperature.

A common reason for using several sizes of grains in a material is to obtain a close texture, the finer grains being used to fill the interstices between the coarser ones and thus reducing the percentage of voids to a minimum. Figs. 1–3 show the difference between the texture produced by grains of uniform and of different sizes. It will be seen that where uniform grains are employed, the voids are quite large, and that the inclusion of grains of smaller size greatly reduces the proportion of voids ; if a third still smaller size is employed, still less space is left between the particles. A large number of different sizes is not necessary and may be undesirable, as they may produce a more porous mass than if only a few sizes were used. It is merely necessary to have about three different grades or sizes, one coarse, one medium, and one fine.

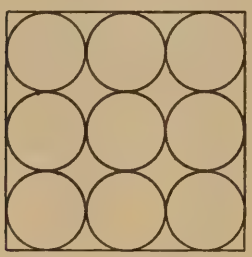


Fig. 1.—Ungraded Mixture.

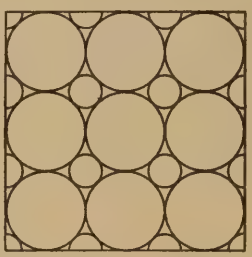


Fig. 2.—Mixture with Two Grades.

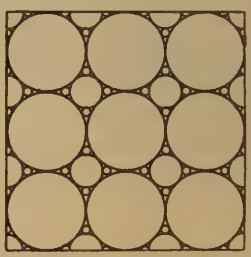


Fig. 3.—Mixture with Three Grades.

These, when combined in suitable proportions, can be made to give a mass of maximum density. The effect of grading has been most thoroughly investigated with regard to concrete and the results of these investigations may be applied with great advantage in the manufacture of articles from clay and refractory materials. In concrete, the coarse stone or aggregate forms the bulk of the solid matter ; between the pieces of coarse material are interstices or voids of considerable size. These are filled with smaller pieces of stone or similar material, but the latter still leave further voids between them. These voids are, in turn, filled with still finer material, such as sand, so that when the cement is added, the whole forms a dense and compact mass. It is possible to make concrete with stones of uniform size, but such a material requires an excessive amount of cement, and the product is weak. It is far better to start with the larger stones and to fill the voids with progressively smaller pieces, until sand, and eventually lime or Portland cement is used, the particles of which are all less than 0·003 inch in diameter. In short, a properly made concrete approaches an ideally graded material.

Taylor and Thompson have found that the proportions of grains of different sizes

will, if plotted in the form of a graph, take the form of an ellipse for the small grains and a straight line joining the ellipse at a tangent for coarse particles.

An ideal graph of this kind for dealing with crushed material and screenings may be constructed from the following data :—

Intersecting tangent with vertical at zero diameter .	29·0
Height of tangent point	36·1
Axes of ellipse : a	0·147D
„ „ $b+7$	37·8

To construct the graph a is found by multiplying 0·147 by the maximum size of the coarse particles and the resultant figure is marked on the horizontal scale of sizes of particles. A vertical line through this point forms axis b of the ellipse. The value b is given above, and the length of the vertical axis is laid with its centre 7 per cent. above the horizontal line of the graph. The ellipse is then complete and the straight line drawn from the point of intersection of the 100 per cent. line and the line denoting the largest-sized particles to a point representing the point of intersection of the tangent with the vertical at zero diameter, the value for this being given above.

The importance of grading materials for making bricks, tiles, pottery, refractory goods, etc., has not been sufficiently realised in this country and is the cause of a large proportion of the difficulties which arise. It is practised extensively on the Continent, with the result that some Continental articles are far more durable than those made in this country.

Materials Producing a Fine Texture.—From the statements in the preceding pages it will be realised that for a material to have a fine texture it must be composed of very small grains, which are, in most cases, united by a bond or cement composed of still smaller grains. The texture will be found to depend upon (*a*) the smallness of the grains of material, whether aggregate or bond, and (*b*) the grading of the material, *i.e.* the proportions of grains of different sizes, and especially the smallest ones which, under some conditions, will cover the others. Thus, a fine-grained, well-graded material will give a smooth, close texture which will be resistant to corrosion, abrasion, etc., whilst a material composed of grains of uniform size, even though they are small, will give a more open and rougher texture which will be more easily corroded and abraded, but is less liable to spall when the material is exposed to sudden changes of temperature.

Fine-grained materials sometimes exist naturally as clays and some other rocks, or they may be produced artificially from materials which have been reduced to a fine powder by grinding. As such treatment is costly, the natural, fine-grained materials are preferred when they can suitably be used.

The best qualities of china clay and kaolin—one of the purest forms of clay—are extremely fine and, with the aid of water, may be passed entirely through a 200-mesh sieve. A large proportion of such material is so fine that it will be carried away by a stream of water flowing at the rate of only 0·18 mm. per second or 0·43 inch per minute. Such grains do not exceed 0·01 mm. in diameter. The finer qualities of

ball clay consist of equally small particles, but they are more plastic than china clay or kaolin. Some ball clays are much coarser. Many other plastic clays chiefly consist of very fine clayey material practically free from coarse matter, most of the grains passing readily through a 200-mesh sieve. Most alluvial clays have an extremely fine texture on account of the manner in which they have been formed. The particles composing fireclays are usually rather coarser than those of ball and china clays, but most will pass through a 100-mesh sieve and a large proportion is carried away by a stream of water flowing at the rate of 0·18 mm. per second. Most of the clays used in the manufacture of bricks and tiles are composed of much larger grains than the best china and ball clays and usually consist of a natural mixture of sand and clay in very variable proportions as well as an indefinite proportion of organic matter. Some good brick clays only contain 50 per cent. of material which will pass through a 200-mesh sieve. Many clays contain a large proportion of silt, which may be defined as consisting of grains between 0·025 and 0·01 mm. in diameter, though natural " silt " and " warp " also contain a considerable proportion of still finer grains of clay. It is not easy to judge the fineness of a clay by inspection, or even by mixing the material with water and then sieving it, because, whilst some clays when mixed with water may readily be disintegrated into their individual grains, others are much more compact and require boiling in water or even the addition of a small quantity of ammonia or other dispersing agent.

Rock clays, shales, fireclays, and some other clays have an extremely fine texture if the individual particles can be separated, but unless special methods are adopted, each " particle " of clay separated by the action of water will be found, on examination, to consist of an aggregation of smaller grains. Articles made of such clays often have a coarser and more open texture than those made from clays in which the individual grains are readily separated from each other.

Freshly dug clays may be classified according to their texture as (*a*) shales, (*b*) marls, (*c*) loams, (*d*) stony clays, (*e*) plastic clays. *Shales* have a laminated or stratified texture (see p. 22). They may be either fine or coarse and either rich or poor in clay, as the term " shale " has no connection with the size of the grains nor with the composition of the material.

Marls or *Malms* are natural mixtures of clay and chalk and may usually be recognised by their friable nature, their texture being quite different from that of other clays. The term " marl " is often used for materials having a similar texture, but which contain very little, if any, chalk, *e.g.* Staffordshire marls. The greater part of most true marls can usually be washed through a 100-mesh sieve, though coarser marls are also found.

Loams are mixtures of sand and clay ; they are largely used for the manufacture of bricks, roofing tiles, floor tiles, terra cotta, agricultural pipes, and coarse (red) pottery. Their texture is similar to that of marls. Loams and marls are often confused, but they may be readily discriminated by adding a little hydrochloric acid, when a marl will effervesce, whilst a loam will not do so. The texture of many loams is such that they are excellent for the manufacture of the articles just mentioned. The sand in them prevents loams from shrinking excessively and enables

articles made from them to be dried and burned without undue risk of cracking or warping.

Some loams contain so much sand that they cannot be used unless they are mixed with plastic clay to enable them to produce a stronger mass. Any very coarse, non-plastic material such as pebbles and gravel in a loam must either be removed or crushed so fine that they will not do any harm when the loam is made into articles.

Stony clays usually consist of fine clay or loam mixed with stones, pebbles, or similar non-plastic material of any size from $\frac{1}{4}$ inch in diameter to large boulders. Much of the " boulder clay " which forms part of the Glacial Drift is of this nature. The coarse material must be separated from the clay or loam before the latter can be used, even for brickmaking.

Plastic clays, when suitably moist, possess a smooth oleaginous texture which is often so fine that no definite " structure " can be seen with the naked eye. If the material is rather drier it can be seen to consist of adherent granules, but many of these appear to be much larger than the particles of clay really are, for the granules consist of aggregations of the much smaller particles of clay. Most plastic clays also contain a considerable proportion of sand and some (such as boulder clay) contain large stones. The causes and nature of plasticity are considered in Chapter VI.

An excessively fine texture is objectionable, because it is usually associated with a tendency to twist or warp when the articles are being dried or burned and with an undue sensitiveness to sudden changes in temperature. For the same reason, loams are often preferable to finer clays, though too much importance must not be attached to this, because earthenware and china are made from very fine-textured materials. To avoid the difficulties caused by an excessively fine texture, a suitable proportion of coarser matter must usually be present in the crude clay or other materials used. The properties allowable will, of course, be dependent on the nature of the ware to be made and on the plasticity, binding power, etc., of the clay itself. Some clays can stand the addition of quite a large proportion of coarser, non-plastic material, whilst others can only carry a very small proportion. It is not possible to judge how much coarser material may be present except by actually testing the materials.

The following definitions have been suggested by Seger for distinguishing the various components of clay and these figures are usually adopted by other investigators :—

Clay includes all grains with a diameter less than 0·01 mm. washed out by a stream of water with a velocity of 0·18 mm. per second under a pressure head of 20 mm.

Silt includes all grains between 0·01 mm. and 0·025 mm. diameter, washed out by a stream of 0·7 mm. velocity per second.

Dust sand includes all grains from 0·025 to 0·04 mm. diameter which are washed out with a stream of water with a velocity of 1·5 mm. per second.

Fine sand includes all grains between 0·04 mm. and 0·33 mm. diameter separated by means of sieves.

Coarse sand includes all particles with a diameter greater than 0·33 mm.

On account of the small grains of which clay consists, an article made of clay

alone will have the properties of a fine-grained material, namely, (*a*) low porosity and great compactness; (*b*) low permeability; (*c*) uniform texture and structure; (*d*) great mechanical strength; (*e*) low resistance to sudden changes of temperature; (*f*) greater resistance to corrosion and abrasion than some coarser amorphous materials. As some of these properties are undesirable in certain kinds of ware, an admixture of a material composed of larger grains is often required. This must be selected with skill, as all coarse materials are not equally suitable. Some form of crushed silica rock or sand is often used, but the most generally suitable material for mixing with clay is burned clay or grog (*below*).

When articles made of materials other than clay are too fine in texture, it is not usually difficult to obtain larger pieces of the same raw material or to avoid crushing it excessively.

The texture of burned clay is much coarser than that of the raw clay, as in the burning the minute grains are aggregated together into a compact mass. Hence, by burning the clay and then crushing the resultant grog, a material composed of pieces of any desired size may be obtained without changing the composition of the material of which the articles are made. Coarse material such as grog is very valuable in making refractory articles, as where it is used as one of the ingredients, the resultant ware is much less sensitive to sudden changes of temperature than when raw clay only is employed. The addition of grog also reduces the shrinkage of the clay.

Materials Producing a Coarse Texture.—When large grains or particles are united by a relatively small proportion of bond or cement, the texture of the material may be described as "coarse." Consequently, the materials used to produce a coarse texture consist chiefly of (*a*) relatively large grains or agglomerations of grains, and (*b*) the cement or bonding agent (if any) which unite them. The bond is almost invariably composed of very small particles and is fine in texture.

The larger grains are usually obtained by crushing masses of suitable material and separating those which are of the desired size by means of sieves or screens. Apart from clay, almost any of the materials considered in this volume may be prepared in this manner, and even clay can be obtained in large pieces which will not produce a fine texture if it is first burned and converted into "grog."

The sizes of the coarser particles naturally depends on the purpose for which the material as a whole is to be used. In bricks, it is usually permissible to have not more than about 10 per cent. of pieces $\frac{1}{8}$ inch diameter, and in gas-retorts a much larger proportion of coarse material (grog) is desirable. For these and other articles the material for producing a coarser texture may be of all sizes from that of coarse sand to pieces $\frac{1}{4}$ inch or, very occasionally, even greater diameter.

Materials for producing Medium Texture.—The majority of the articles made from clay and other ceramic materials require to have a medium or rather finer texture. To produce this, they must consist of a mixture of particles of at least two sizes, namely, "medium," which may be between 0·08 and 0·01 inch and "fine" particles which are less than 0·01 inch in diameter. Unless the materials used provide the desired texture naturally, they must be ground and screened in such a manner that pieces of unsuitable size are separated. In the case of bricks,

tiles, and other clay ware, the fine material is usually clay, the medium being either sand or grog, which has previously been screened to provide pieces of the required size. When sand is mixed with clay for brickmaking, etc., it should usually consist of grains between 30- and 120-mesh. The use of much coarser grains is undesirable, as it prevents sharp corners and edges being produced on the articles. The grains of sand or other coarser material should never be sufficiently large to project from the surface of the ware.

Large grains of sand and other forms of silica are also undesirable, because they usually expand when heated, even after they have been in use some time. This is due to the fact that, being large, they are not readily converted to the low-specific gravity forms of silica and, consequently, they continue to expand every time they are heated and in so doing often cause much trouble.

Texture of Ceramic Articles.—In the manufacture of *bricks*, *roofing tiles*, *terra-cotta*, *drain pipes*, and *coarse pottery*, the "clay," when prepared for use and then made into a slurry with water, should pass completely through a 24-mesh sieve. For bricks, a rather coarse material will usually suffice, but for the other articles mentioned a coarse "clay" is objectionable. For pottery, the "clay" should usually be fine enough to pass completely through a 50-mesh sieve and for very fine earthenware and porcelain it should pass through an 80-mesh sieve after the material has been mixed with sufficient water to form a slip or slurry.

For *firebricks* and other refractory articles, the proportion of fine grains should not be excessive or the goods may not be sufficiently resistant to heat. In the case of clay wares, there must, however, be sufficient fine particles to provide the necessary bond and the same is true, though in a somewhat different sense, with regard to articles such as silica bricks, magnesia bricks, etc., made of non-plastic materials. In some cases, however, in order to meet special conditions, it is necessary to sacrifice some of the refractoriness in order to obtain other necessary properties and a larger proportion of fine material may then be used.

The relative fineness or coarseness thus depends on the purpose for which the articles are to be used and the conditions to which they are likely to be subjected. Particles of grog used in making clay wares vary in size from 0·25 inch to 0·025 inch diameter, according to the article required and the conditions under which it is likely to be used. Some manufacturers use all the grog which passes through a 10-mesh sieve, but this is undesirable as it includes all the dust. A better method is almost the reverse of this, namely, to exclude all the material which passes through a 16-mesh sieve. In making saggers it is convenient to use three sizes of grog, namely, (*a*) *coarse grog*, consisting of particles between $\frac{1}{8}$ inch and $\frac{3}{8}$ inch diameter; (*b*) *medium grog*, consisting of particles between $\frac{1}{16}$ inch and $\frac{1}{8}$ inch diameter; and (*c*) *fine grog*, consisting of particles between $\frac{1}{32}$ inch and $\frac{1}{16}$ inch diameter. Very coarse grains are necessary in saggers, as it is specially important that they should be resistant to sudden changes of temperature, because, when in use, they are exposed to the flames as well as to eddies of hot gas and cool air and are repeatedly heated and cooled, so that they have to resist conditions much more stringent than most other wares. Under such circumstances, coarse grog will give a greater durability,

but it should not be excessively coarse or it will unduly reduce the strength of the saggers. The best mixture is a graded one, consisting of both coarse and medium particles, as this combines the necessary strength with the requisite resistance to sudden changes of temperature.

The sizes of particles used by different firms vary according to the nature of the materials and the texture which has been found in practice to be most satisfactory. Thus, one well-known manufacturer of refractory goods classifies his grog into the following divisions : (*a*) 5-mesh to 10-mesh, and (*b*) 10-mesh to 20-mesh ; whilst in another works the " coarse " grog consists of particles between 0·25 inch and 0·15 inch diameter, and the " fine " grog consists of particles less than 0·08 inch diameter.

The surface of refractory bricks should be as smooth as possible, especially where they are subject to the action of corrosive substances, which more easily attack rough-surfaced bricks than those with a close texture. This smoothness can only be obtained if the material of which the bricks are made contains sufficient fine clay. The smallest particles of clay tend to flow to the surface during the process of manufacture, and then produce the fine surface-texture or " skin " which is so desirable when the bricks must resist corrosion and abrasion.

The durability of firebricks and of other articles subjected to abrasion or corrosion depends largely on the texture. A fine-textured material will, under ordinary conditions, be the most durable, because the action of the corrosive material will be confined so much more to the surface that it will act much more slowly than it would on an article of the same material but composed of coarser particles. When a corrosive or abrasive agent attacks a coarse-textured brick or other article, it loosens and eventually separates the larger pieces, so that they fall out, leaving relatively large gaps. This is clearly impossible with a fine-textured material. Many firebrick manufacturers tend to make their bricks of too coarse a material in order to make them resistant to sudden changes of temperature, but this is always at the expense of the durability in other directions.

Large blocks may usually be of coarser texture than bricks, on account of their size and the slowness with which heat passes through them. For fireclay blocks about 50 per cent. of grog between 4- and 20-mesh should usually be employed, and all fine powder other than fireclay should be scrupulously avoided. Even a small proportion of fine grog is harmful where the articles are required to resist temperature changes, but where they are only to resist compression fine grog is an advantage, as it produces a stronger mass. Careful grading is especially necessary when making the larger size of blocks, as if proper attention is not paid to this point the blocks will be too sensitive to sudden changes of temperature. Badly graded mixtures are very liable to spall and crack when repeatedly heated.

Muffles must be made with as coarse-grained a texture as possible so as to resist the sudden changes of temperature to which they are subjected. They must not be too coarse, however, as they are required to have sufficient strength and durability in use, though strength is not so important as in saggers. An excessively coarse texture is undesirable as the muffle may be subjected to the corrosive influences of dust and fire gases, especially if the fuel is not of very good quality.

Retorts should be coarse-grained in order to secure a maximum refractoriness and resistance to temperature changes. This latter property is especially important, as retorts are often charged with cold material, whilst they themselves are at a very high temperature. An excessively coarse texture in retorts is, however, undesirable, as such a structure is not so strong as a finer one and the thermal conductivity is smaller. In some cases resistance to corrosion is also necessary, and for this a dense texture is very desirable. The best sizes of grog for retorts are between $\frac{1}{4}$ inch and 60-mesh, though the Institution of Gas Engineers specify that none of the grog should pass through a sieve having sixteen meshes per linear inch. This specification, if followed, produces so coarse a texture that the strength of the retorts is very low. Gas retorts in Germany are usually made with two sizes of grains : (*a*) 0·4–0·12 inch, and (*b*) 0·12–0·04 inch, used in the proportion of 7–8 measures of the coarser with 2–3 measures of the finer grog. Smaller grains than those mentioned are not used, as they would unduly increase the density of the mass.

The *glasshouse pots* used for melting glass are required to be (*a*) sufficiently strong to bear the pressure of the molten glass in them ; (*b*) sufficiently resistant to the temperature changes occasioned by the heating and cooling of the pot, especially when it is hot and quickly charged with cold materials ; and (*c*) sufficiently dense to prevent undue corrosion by the glass. Requirements (*a*) and (*c*) are obtained by the use of a fine-textured material, but (*b*) requires a coarse texture, so that a compromise must be made, a suitably graded material being quite satisfactory. For instance, they may consist of particles of grog between 0·25 inch and 0·05 inch diameter, the bulk being between 0·125 inch and 0·10 inch diameter, and the clay being sufficiently fine to pass, when dry, through a 15–16-mesh sieve. In no case should any grains larger than those mentioned be used or the strength of the pots will be unduly reduced. A small proportion of medium or moderately fine grog may be used in glasshouse pots in order to produce a sufficiently strong mass with a compact surface, but as fine grog reduces the resistance to sudden changes of temperature an excess must be avoided.

Glass tank blocks require a similar texture to those of glass pots, but the strength is not so important as there is a greater thickness of material. According to the provisional specification of the Society of Glass Technology, the fireclay flux-line blocks of glass tank furnaces should consist of grains of grog of the following sizes : 1 measure of grains $\frac{1}{8}$ inch to $\frac{1}{10}$ inch, and 2 measures of grains $\frac{1}{10}$ inch to $\frac{1}{32}$ inch in diameter. The grog for the tank bottom blocks should be

1 measure of grains $\frac{1}{4}$ inch–$\frac{1}{8}$ inch.
1 measure of grains $\frac{1}{8}$ inch–$\frac{1}{10}$ inch.
1 measure of grains $\frac{1}{10}$ inch–$\frac{1}{32}$ inch.

For bottom side blocks, 1, 2, and 1 measures are used respectively. For replacement flux-line blocks, 2, 2, and 1 measures are used.

The texture of *crucibles* presents a problem similar to that of glasshouse pots, the conditions of use being, in the main, very similar. Strength is very necessary in large crucibles, as some may hold as much as half a hundredweight of metal which

must be carried in the crucible, sometimes for a considerable distance. When a crucible is lifted out of the furnace it undergoes a sudden change of temperature, so that it must be made very insensitive to temperature changes. These properties are obtained by suitably grading the non-plastic materials used in the manufacture of the crucibles. The interior of crucibles should be finer than the exterior, as the inner surface must be resistant to corrosion by the contents.

Earthenware and *porcelain* are required to have a fine texture, and the materials used in their production are, therefore, ground very fine, with the exception of the clays, which are naturally fine in texture.

The texture of refractory materials other than clay varies according to their mode of formation. Thus, the *siliceous materials* generally used for the manufacture of silica, ganister, dinas, and similar bricks, are usually very fine in texture, though many of the pieces of which the bricks are composed may be relatively large. For instance, some of the best ganister occurs in the Sheffield district, and consists of grains between 0·1 and 0·3 mm. diameter, but the material is only ground to pass through a 24-mesh sieve. In other words, the coarser particles consist of aggregations of much finer ones. Similarly, the bastard ganisters of Durham and North Yorkshire consist of grains between 0·05 and 0·15 mm. diameter as a rule, whilst the Scottish bastard ganisters are extremely fine-grained, consisting chiefly of particles less than 0·1 mm. diameter. The Chwarele ganister of North Wales also has a similar structure. All these are very suitable materials for the manufacture of ganister bricks, but ganisters consisting of grains up to 0·6 mm. diameter are not so satisfactory. It may be assumed that for most purposes a diameter of 0·4 mm. is about the maximum desirable for the individual grains of siliceous material. Silica bricks generally consist of a suitable mixture of the following grades : (*a*) particles between 0·125 inch and 0·25 inch diameter ; (*b*) particles between 0·04 inch and 0·125 inch diameter ; (*c*) fine powder. The proportions in which these materials are mixed depend on the purpose for which the bricks are to be used.

As silica bricks are always sensitive to sudden changes in temperature, no matter how carefully they are made, there is no object in making them coarse-textured or in omitting fine material. On the contrary, the best silica bricks are those in which there is a minimum of voids. This is secured by making the fine grains fill the interstices between the larger particles and the dust should fill the interstices between the fine grains. Equal proportions of each size have proved to be quite satisfactory in some cases and where coarse grains are undesirable equal parts of the two finer grades alone may be employed. The advantage of using fine dust in silica bricks is that (*a*) the interstices between the large grains are partially filled and enable a stronger mass to be produced ; (*b*) some of the dust or flour is converted into the amorphous state and so aids in binding the mass together and when heated reacts more readily with the lime also added so producing a good strong bond ; and (*c*) the fine flour is more easily converted into one of the low specific gravity forms of silica, thus reducing the volume changes in the bricks when in use.

In some cases, fine water-ground flint is added in making silica bricks to supply the required amount of fine material. It has the advantage of being very readily

converted into tridymite. At the same time, an excess of impalpable silica is undesirable as a general rule, as it readily combines with fluxes and so reduces the refractoriness of the bricks.

A well-graded material is specially important in making silica bricks, because only about 2 per cent. of lime is allowable for bonding purposes and if the silica is badly graded a larger proportion of lime will be necessary. The use of a sufficient proportion of fine material greatly increases the strength of silica bricks. If they are made wholly of fine natural (*flour*) the maximum strength is obtained, but the bricks are unduly sensitive to sudden changes of temperature. By using a smaller amount, however (about 30 per cent.), Phillipon found that a high strength could be obtained without the drawback just mentioned. According to H. Le Chatelier and B. Bogitch,[1] not more than 25 per cent. of grains smaller than 200-mesh should be present in silica bricks. As showing the harmful effect of excessively fine material, it should be noted that the grains produced by crushing calcined flint are generally very small and are not aggregated together as in ganister, silica rock, etc., so that bricks made from them are too sensitive to sudden changes of temperature.

The texture of *sand-moulds* used in foundry work is very important, as on it depends very largely the quality of the castings produced in the moulds. To ensure good castings the texture much be such that the moulds will have (*a*) a fine surface texture, so as to produce a smooth surface on the castings ; (*b*) ample permeability and porosity, to enable all air and gases to escape through the pores of the mould as rapidly as possible ; (*c*) ample strength to withstand the pressure of the molten metal, which is often very great and is applied very suddenly ; and (*d*) the sand used for the moulds must contain sufficient colloidal or equivalent fine material to enable a sufficiently plastic mass to be formed by the addition of only a small proportion of water. The first and last desiderata are obtained by the use of sand composed of fine grains, including some clay, whilst the remainder require a coarse-grained sand. Consequently, in selecting a moulding sand, a compromise must be effected, the proportions of coarse and fine grains being varied according to the kind of castings required. In a very large casting, for example, the strength and permeability of the mould are more important than a smooth surface, so that a coarse-grained sand should be employed ; whilst in a very small casting, the strength of the mould is unimportant, but smoothness of finish is of the greatest importance, and to secure this a fine-grained sand must be used. To ensure ample permeability, all the grains in a moulding sand should be as nearly uniform in size as possible and should generally be between 0·25 and 0·5 mm. diameter for medium work, and between 0·1 and 0·25 mm. for fine work and facing purposes. According to R. L. Lindstrom, the moulding sands used in casting steel should not contain more than 5 per cent. of grains larger than 20-mesh (0·64 mm.), and not less than 75 per cent. of grains larger than 100-mesh (0·125 mm.). Grains of uniform size impart a less regular and smooth surface than mixtures containing grains of various sizes, and as they cannot interlock they do not produce a mass having the maximum strength, but the deficiency in smoothness may

[1] *Rev. de Mét.*, **15**, 511 (1918).

usually be overcome by the use of a fine "facing coat" and the strength may be increased by various mechanical devices when designing the moulds.[1]

Furnace hearths made of refractory sands should have a close, dense texture so as not to absorb an unnecessary amount of metal and slag, and the individual grains should be sufficiently small to be converted as quickly as possible into the low specific gravity forms of silica (cristobalite and tridymite). The sands used for lining the hearths of open-hearth furnaces in this country usually consist of grains between 0·25 mm. and 0·5 mm. in diameter, but coarse material is sometimes used. Some of the Greensand beds which are used for this purpose consist almost wholly of grains of the above-mentioned sizes. In the Leighton Buzzard sand there is, according to Boswell, about 24 per cent. of grains larger than 0·5 mm. diameter and 74 per cent. between 0·25 mm. and 0·5 mm. diameter. The Aylesbury sand is somewhat finer, and contains more than 78 per cent. of grains between 0·25 mm. and 0·5 mm. diameter, about 15 per cent. between 0·1 mm. and 0·25 mm. diameter and 6 per cent. between 0·01 mm. and 0·1 mm. diameter. In the United States, coarser sands, consisting of grains up to 10-mesh or even to 5-mesh, are regarded as satisfactory, though they involve larger loss of metal by absorption. American steel makers rightly consider that fine-grained sands are undesirable in open-hearth furnaces, because they have only a small angle of rest, whereas the bank of these furnaces should be as steep as possible; such sands are also undesirable on account of the ease with which the smaller grains fuse superficially, but most British steel makers who have given attention to the subject consider that in their endeavour to avoid the use of sands of too fine a texture, the Americans have gone too far towards the other extreme of excessively coarse-textured linings.

When repairing furnace linings it is customary to throw the sand on to the defective portions and it is, therefore, important to use a sand or mixture which will naturally produce a material of the desired texture under such crude conditions. If the grains of sand are all uniform in size they will, when thrown into the furnace, fall or roll into the required position and will readily produce a mass of maximum density, whereas a sand composed of grains of various sizes will, in the absence of any tamping or ramming, form a mass with a more porous and irregular texture and, therefore, less satisfactory.[1]

The texture of magnesite to be used for *magnesia bricks*, etc., should be that produced by coarse crystals, as these produce an open or porous mass which is more readily calcined than one having a finer and denser texture, such as crypto-crystalline magnesite; the latter requires a higher temperature as well as more prolonged heating, to ensure it being completely "dead-burned." The coarse crystalline texture of some forms of magnesite also facilitates the removal of impurities such as serpentine, quartz, etc., which are difficult to remove from the finer-grained, crypto-crystalline magnesite, yet if they are not separated they reduce the refractoriness of the material. Magnesite spar and breunnerite are usually coarse-grained, whilst the

[1] Further information on the use of sands for casting metals and for lining furnaces will be found in the author's *Sands and Crushed Rocks: Their Nature, Preparation, and Uses* (Frowde, Hodder & Stoughton).

grains of crypto-crystalline magnesite and hydromagnesite are of microscopical dimensions.

The texture of magnesia bricks, blocks, etc., should be "medium," only just sufficient fine material being present to provide the necessary bond for the larger particles. To produce this texture, the dead-burned magnesia should be crushed and screened so as to remove all particles larger than $\frac{1}{16}$ inch diameter and all those smaller than 50-mesh. Coarser particles will require too long a heating to convert them into periclase. The fine particles constituting the bond should be as small as possible, so that they may offer a large surface to the grains of magnesia. If the fine grains consist chiefly of iron oxide, they will act as a catalyst and assist in converting the amorphous magnesia into periclase. An excessive proportion of fine grains should be avoided, or the bricks, etc., will crack or "dunt" when exposed to sudden changes in temperature.

The texture of *dolomite bricks* is usually that due to the use of particles of dolomite less than $\frac{1}{4}$ inch diameter, about 25 per cent. of the grains being smaller than 100-mesh. An excess of fine grains is undesirable, as it renders the bricks too sensitive to sudden changes of temperature.

In order to produce a satisfactory texture in the *dolomite linings* of Bessemer steel converters, the ground dolomite used should not contain any particles more than 5–6 mm. diameter and about 30–40 per cent. of the material should be in the form of fine grains.

The texture of *bauxite bricks* is usually that produced by particles between $\frac{1}{4}$ inch and $\frac{1}{20}$ inch diameter, united with 15–30 per cent. of finely ground fireclay. Some manufacturers prefer to use finer bauxite.

The texture of *corundum* articles used for refractory purposes should be as coarse as the conditions of their use will allow, as the larger the crystals the more resistant is the material to sudden cooling and shocks. Granger has recommended the use of 12-mesh grains for carborundum crucibles and a mixture of 4- to 5-mesh grains and 7-mesh grains for tubes and similar articles. It is usually advisable to make corundum bricks of 7 parts of coarse crystals of corundum, 1 part corundum in fine powder, together with 1 part of plastic fireclay to bind the other particles together.

The texture of *coke bricks* is produced by the use of particles 0·04 to 0·08 inch diameter, bonded with gas-tar or soft pitch. On burning, the tar is coked, forming a strong bond. Bricks made of plumbago bonded with fireclay have very fine-grained texture on account of the nature of the materials used, but as the mixture undergoes a negligible change in volume when the bricks are in use, the close texture does not interfere with the resistance of the bricks to sudden changes in temperature, whilst it has the advantage of rendering them more resistant to corrosion and of increasing their thermal conductivity.

The so-called *graphite slabs* used for flattening window glass require to be specially resistant to repeated changes of temperature; they are, therefore, made with a coarse texture, the materials used consisting of particles of grog and graphite up to 10-mesh and fireclay up to 28- or 30-mesh. The surface of these slabs is usually covered with (or has the upper surface to a depth of $\frac{1}{4}$ inch made of) a material of

rather finer texture, all the particles used for this portion being capable of passing through a 25-mesh sieve.

The texture of *carborundum bricks* is not usually of great importance, as carborundum is insensitive to sudden changes in temperature and very largely so to corrosion. The material should, however, be graded so as to form a sufficiently strong mass. In one of their patent specifications, the Carborundum Company state that the grains for carborundum bricks should be between 16- and 100-mesh, a suitable mixture consisting of equal parts of 16-, 24-, 36-, and 100-mesh, together with some fine powder if desired.

The texture of *cements* should be extremely fine, so that the individual particles will have as large a surface as possible and the necessary bonding power. In refractory cements, the particles should be small enough to fuse superficially and so produce a strong binding agent and yet should be sufficiently large to have the requisite refractoriness. It is customary to grind refractory cements until they pass entirely through a 24-mesh sieve, but such a material is coarser than is desirable. If it is made to pass through a 60-mesh sieve it will give better results, and if ground to an impalpable powder it will be still better. The coarse particles are useless in a cement, as they have very little binding power, so that it is always desirable to use cements which have been ground to as fine a state of division as possible, having due regard to the expense of very fine grinding. For most purposes, if a refractory or similar cement does not leave a residue of more than 10 per cent. on a 200-mesh sieve, there is little to be gained by grinding it still further.

Determining the Texture.—If an article or mass of material has a coarse texture, this may be seen by the naked eye or with the aid of a small magnifying glass, but a medium or fine texture requires a microscope for its examination. The texture is more easily seen if the material is ground flat and then polished, or even if, as suggested by J. Lomas, it is ground fairly smooth and a thin sheet of clear glass is cemented to it by means of Canada balsam. A simple lens may be used for examining a comparatively rough surface, but if a microscope is to be used effectively the variations in the surface must not be so great that some portions are out of focus, whilst others are clearly visible. It is a mistake to use too powerful a microscope when examining the texture of a material; a medium magnification (not exceeding 120 diameters) is best, the greater magnifications being reserved for the examination of individual particles rather than the texture as a whole. If required, the size of the particles may be measured by means of a microscope and an eyepiece micrometer.

If a material is easily disintegrated into its component particles, as when dried clay is rubbed between the fingers or stirred with a larger quantity of water, useful information respecting its texture may be obtained by one or more of the four following methods in which the particles of different sizes are separated from each other: (*a*) screening, riddling, or sieving (p. 45); (*b*) elutriation (p. 50); (*c*) air separation (p. 53), and (*d*) sedimentation (p. 53).

The first method is suitable for separating all particles larger than 0·0025 inch diameter; the others are chiefly suitable for smaller particles. A combination of method (*a*) with either (*b*) or (*d*) is sometimes termed *mechanical analysis*. All four

methods are equally applicable to determining the sizes of the grains of various loose materials and powders.

Screening, riddling, or sieving consists in passing the material—either in its dry state or in suspension in water—over screens, riddles, or sieves having various apertures of known dimensions. The particles larger than these apertures remain behind, whilst the smaller particles pass forward and will be retained by the successively smaller apertures until the last sieve is reached, through which the smallest grains will eventually pass. This method is very convenient for separating all particles larger than 0·0025 inch diameter (200-mesh), but is seldom applicable to smaller ones on account of the difficulty of making accurate sieves with smaller apertures.

Sieves, riddles, and screens are made with apertures of various shapes, some apertures being circular, others square, and still others being rectangular. The last-named are useless for investigating the texture or fineness of a material. Sieves with circular apertures do not give the same results as those with square ones, and the results obtained with a sieve made of perforated sheet will differ from those of a sieve made of wire-gauze and having square apertures. The latter are generally employed for testing purposes.

Gauze sieves are made of various metals, including iron, steel, brass, bronze, and occasionally copper. In some cases, gauzes made of silk are employed for the finest materials, but they are very delicate and not to be recommended. Those made of phosphor-bronze are usually the most satisfactory. All sieves used for testing should be examined to ensure the apertures all being of the desired sizes, as otherwise the results obtained may be erroneous. Such sieves should be very carefully used, especially the finer ones, as they are soon spoiled if used for material much coarser than the mesh of the sieve. For instance, no material coarser than 50-mesh should be put on to a 100- or 200-mesh sieve ; the larger particles should have been separated previously by passing the material through coarser sieves. Fine sieves which have been in use for some time may permit particles larger than the nominal mesh of the sieve to pass through them on account of the wear of sieving the material and of the stretching and sagging of the wires. For this reason the mesh of such testing sieves should be examined from time to time and, if any apertures are too large, the sieve should be repaired or discarded. In order that all results obtained when testing the texture or fineness of a material by means of sieves may be comparable, it is most desirable that " standard sieves " should be employed, otherwise the size of grains corresponding to a given sieve may not be known, and the results, if reported, will be of little use except to the original user, and may cause confusion. The standard for sieves used in this country is that adopted by the Institute of Mining and Metallurgy ; [1] the relation of aperture to thickness of wire and mesh-number are shown in Table I.

In other countries, different standards are used ; the one generally recognised in America is that suggested by the U.S. Bureau of Standards,[2] with the dimensions shown in Table II.

[1] Such sieves are made by N. Greening & Son, Warrington.

[2] These sieves are made by the W. S. Tyler Co., Cleveland, Ohio, U.S.A.

On the Continent, it is usual to refer to sieves by the number of apertures per square centimetre. The relation of these to British sieves is shown in Table III.

In order to convert the results obtained with a sieve expressed by the number of holes per sq. cm. into the British sieve number, the square root of the Continental figure should be multiplied by 10 and divided by 4. Thus, for a sieve having 400 holes per sq. cm., the square root of 400 is 20, which, multiplied by 10 and divided

TABLE I.—*I.M.M. Standard Sieves*

Mesh, *i.e.* Apertures per linear inch.	Diameter of Wires.		Diameter of Apertures.		Screening Area per cent. holes.
	inch.	mm.	inch.	mm.	
5	0·1000	2·540	0·1000	2·540	25·00
8	0·0630	1·600	0·0620	1·574	24·60
10	0·0500	1·270	0·0500	1·270	25·00
12	0·0417	1·059	0·0416	1·056	24·92
16	0·0313	0·795	0·0312	0·792	24·92
20	0·0250	0·635	0·0250	0·635	25·00
30	0·0167	0·424	0·0166	0·421	24·80
40	0·0125	0·317	0·0125	0·317	25·00
50	0·0100	0·254	0·0100	0·254	25·00
60	0·0083	0·211	0·0083	0·211	25·00
70	0·0071	0·180	0·0071	0·180	25·00
80	0·0063	0·160	0·0062	0·157	24·60
90	0·0055	0·139	0·0055	0·139	24·50
100	0·0050	0·127	0·0050	0·127	25·00
120	0·0041	0·104	0·0042	0·107	25·40
140	0·0036	0·091	0·0036	0·091	25·00
150	0·0033	0·084	0·0033	0·084	24·50
160	0·0031	0·078	0·0031	0·078	25·00
180	0·0028	0·071	0·0028	0·071	25·00
200	0·0025	0·063	0·0025	0·063	25·00

by 4, gives 50. This sieve, therefore, corresponds to one having 50 meshes per linear inch, *i.e.* to a No. 50, or 50-mesh sieve.

Unless British, American, or other standard sieves are used the size of the apertures cannot be calculated from the mesh-number, as so much depends on the gauge of the wires used. For instance, two sieves may each have 10 holes per linear inch, but whilst in one the holes may be 0·05 inch in diameter and the wires 0·05 inch thick, in the other the holes may be of 0·067 inch in diameter and the wires 0·033 inch. It is, therefore, most important either to use sieves of standard design or to specify

the actual dimensions of the apertures as ascertained by direct measurement, so that the maximum size of grains passing through a sieve of any particular size may be accurately known.

TABLE II.—*American Standard Sieves*

Sieve No.	Sieve Opening.	Sieve Opening.	Wire Diameter.	Wire Diameter.	Tolerance in Average Opening.	Tolerance in Wire Diameter.	Tolerance in Maximum Opening.	Mesh per cm.	Mesh per inch.
	mm.	inches.	mm.	inches.	per cent.	per cent.	per cent.		
$2\frac{1}{2}$	8·000	0·3150	1·850	0·0730	1	5	10	1·0	2·6
3	6·720	0·2650	1·650	0·0650	1	5	10	1·2	3·0
$3\frac{1}{2}$	5·660	0·2230	1·450	0·0570	1	5	10	1·4	3·6
4	4·760	0·1870	1·270	0·0500	1	5	10	1·7	4·2
5	4·000	0·1570	1·120	0·0440	1	5	10	2·0	5·0
6	3·360	0·1320	1·020	0·0400	1	5	10	2·3	5·8
7	2·830	0·1110	0·920	0·0360	1	5	10	2·7	6·8
8	2·380	0·0940	0·840	0·0330	2	5	10	3·0	7·9
10	2·000	0·0790	0·760	0·0300	2	5	10	3·5	9·2
12	1·680	0·0660	0·690	0·0270	2	5	10	4·0	10·8
14	1·410	0·0557	0·610	0·0240	2	5	10	5·0	12·5
16	1·190	0·0468	0·540	0·0210	2	5	10	6·0	14·7
18	1·000	0·0394	0·480	0·0187	2	5	10	7·0	17·2
20	0·840	0·0331	0·420	0·0165	3	5	25	8·0	20·2
25	0·710	0·0278	0·370	0·0146	3	5	25	9·0	23·6
30	0·690	0·0234	0·330	0·0129	3	5	25	11·0	27·5
35	0·500	0·0197	0·290	0·0113	3	5	25	13·0	32·3
40	0·420	0·0166	0·250	0·0098	3	5	25	15·0	37·9
45	0·350	0·0139	0·220	0·0085	3	5	25	18·0	44·7
50	0·300	0·0117	0·188	0·0074	4	10	40	20·0	52·4
60	0·250	0·0098	0·162	0·0064	4	10	40	24·0	61·7
70	0·210	0·0083	0·140	0·0055	4	10	40	29·0	72·5
80	0·177	0·0070	0·119	0·0047	4	10	40	34·0	85·5
100	0·149	0·0059	0·102	0·0040	4	10	40	40·0	101·0
120	0·125	0·0049	0·086	0·0034	4	10	40	47·0	120·0
140	0·105	0·0041	0·074	0·0029	5	15	60	56·0	143·0
170	0·088	0·0035	0·063	0·0025	5	15	60	66·0	167·0
200	0·074	0·0029	0·053	0·0021	5	15	60	79·0	200·0

When the texture or fineness of a material is to be examined by means of a sieve, the material may be used either in the dry state or after it has been mixed with a large amount of water. The former is sometimes termed a " sieving " or " screening "

test, and the latter a " washing test." Whilst the results obtained are quite different, the method of using the sieves is very similar in each case.

For a (dry) sieving test, a weighed quantity of the material (*i.e.* 100 oz. if it is very coarse) should be rubbed gently between the finger and thumb or with a smooth wooden pestle, taking great care not to crush the individual grains but only to separate them from one another. When the material has thus been reduced to a rough " powder " it is placed on the coarsest sieve and either stirred or shaken gently until as much of it as will pass through the sieve has done so. The residue is examined to ensure the absence of aggregations of smaller grains which have escaped the rubbing, and when these (if any are present) have been broken down, and passed through the

TABLE III.—*Relation of Various Sieves*

No.	Meshes per linear inch.	Meshes per square inch.	Meshes per cm.	Meshes per square cm.
30	30	900	12	144
60	60	3,600	24	576
90	90	8,100	36	1,296
100	100	10,000	40	1,600
120	120	14,400	48	2,304
150	150	22,500	60	3,600
200	200	40,000	80	6,400

sieve, the residue on it is weighed. The material which has passed through the first sieve is similarly treated on the next finer sieve in the series, and this process is continued until all the sieves have been used.

The weights of the various residues, together with that of the material which has passed through the finest sieve, should be equal to the weight of the original mass. If any appreciable difference occurs some of the material has been lost in the process.

It is not always necessary to use all the sieves, and for many purposes it is sufficient if the aperture in each of the sieves used is about half that of the one preceding it. Thus, for most clays and similar materials the following sieves will suffice: Nos. 3, 6, 12, 25, 50, 100, and 200, the intervening ones only being used for special purposes.[1]

[1] Mellor has suggested that in most cases three sieves of 5-, 50-, and 120-mesh are sufficient, whilst Boswell prefers to separate materials into the following divisions :—

Greater than 2 mm. diameter.
1–2 mm. diameter.
0·5–1 mm. ,,
0·25–0·5 mm. ,,
0·1–0·25 mm. ,,
0·05–0·1 mm. ,,
0·01–0·05 mm. ,,
Less than 0·01 mm. diameter.

Unless a material is almost or quite dry, a dry sieving test will not yield satisfactory results, and a washing test should then be employed.

For a *washing test* a small or larger weight of material is used according to the nature of the substance. If it is fairly fine and uniform, 500 grams is ample and even 200 grams may be sufficient, but for coarse, heterogeneous material it is more convenient as well as more accurate to use 100 oz. ($6\frac{1}{4}$ lb.) or 3 kilograms. The material should be dried before being weighed, or a separate determination of moisture in it should be made. The weighed material is carefully mixed with about four times its weight of very soft, or perfectly distilled water in a basin of convenient size. Some clays which would be difficult to manipulate at a later stage are made easier if a few drops of ammonia are added and the mixture of clay and water boiled for about ten minutes. In any case, the object is to get all the smaller particles into suspension in the water without breaking up any coarser ones which may be present and without altering the chemical composition of the material. If the material does not readily form a fairly smooth " cream " or slip, the more resistant portions may be gently rubbed with a polished wooden or porcelain pestle to loosen all the particles, or with materials containing much coarse matter of a fragile nature, the fingers may be used to remove the finer particles from the coarser ones. Some " clays " which are difficult to manipulate when freshly wetted can easily be tested if roughly mixed with water and then allowed to stand for twenty-four hours. The liquid containing material in suspension is next run through a sieve, the mesh of which will depend on the size of the largest particles in the sample. This may be ascertained with sufficient accuracy by looking at the portion of the material which sinks to the bottom of the liquid, and from its appearance selecting an appropriate sieve, as there is no advantage to be gained by passing the material through sieves with such large apertures that no residue will be left on them. The slip or slurry thus produced is passed through each of the sieves in turn, each residue being returned to the basin, treated with more water and again transferred to the sieves in turn. This process of treating with water is repeated until the residue on each sieve is " clean " and free from all particles which will pass through the particular sieve on which the particles are supposed to be retained. If necessary, a fine yet powerful jet of water may be directed on to the contents of a sieve so as to wash out any finer particles. During this treatment care must be taken not to break up grains of non-plastic material, or to rub the material so hard that it will be ground and so enabled to pass through the sieves on which it should be retained.

The material which has passed through all the sieves is next received in a large glazed pan, in which it may be left all night, when the greater part of the solid material will have settled. The clear surplus water may be removed by means of a siphon. If, however, the suspended matter does not settle readily, the only means of removing the water is by evaporating the mixture to dryness in a large evaporating basin, heated on a water bath or over a cylinder containing steam. It cannot be boiled dry with safety, on account of its tendency to " spit." As this operation of drying is very tedious and cannot be hurried, there is a great tendency to use as small a quantity as possible of material for the washing test, so as to reduce the time of

evaporation to a minimum. Alternatively, either an aliquot part, or the whole of this material may, if desired, be subjected to an elutriation (*below*) or other test.

The residues on the various sieves are washed into evaporating dishes of convenient size and are dried by heating on water baths, or first over a very low gas flame and then on a water bath or sand tray. They are finally dried at 110° C., or as near to this temperature as is attainable, and are afterwards weighed. The results may be calculated to a percentage by multiplying each by 100 and dividing by the total weight of the material originally used. The total should add up to 100·00, apart from any losses (including any moisture present) which may have occurred. Usually a difference of 0·5 per cent. between two tests of the same sample is regarded as unavoidable, though with uniform materials a smaller error of experiment is possible.

Both skill and care are required when using sieves in the manner described, or some fine material which ought to pass through one or more sieves may be left amongst the coarser matter. This is less likely to occur with dry material if the sieves are covered and agitated mechanically, *e.g.* by a small motor, for a definite time, instead of shaking them by hand. It is also an advantage to connect a series of sieves together, one above another, so that all may be agitated simultaneously.

Elutriation consists in separating particles of different sizes or of different specific gravity by suspending them in a fluid, such as water, which is flowing at such a velocity as will enable it to carry off the smallest or lightest particles, whilst the largest or densest ones settle to the bottom of the elutriating vessel. When used for examining the texture or fineness of a material it is usually assumed that the particles will be separated according to their sizes, but when a heterogeneous material is examined the possibility of relatively large particles of low specific gravity being removed along with the smallest particles must not be overlooked. The shape of the particles also has an important effect on their behaviour during elutriation; grains of a flaky character are carried away by a current of the same velocity as much smaller grains of a more cubical or spherical shape. Other factors which influence the results are (*a*) the purity of the water, as hard water has a flocculating action on some fine clays; (*b*) the temperature of the water, which should be kept constant at 15° C.; and (*c*) the amount of matter in suspension in the elutriator; this should be kept as constant as possible to 10 grams of material actually placed in the vessel, quite apart from the weight of coarse material in the original sample. In order to avoid flocculation of the clay grains, some investigators add a little ammonia to the water used for elutriation; this is an undesirable practice, which should be avoided wherever possible.

If several elutriators are used in series, the liquid in each having a different velocity, it is possible to separate a material into as many "grades" as there are vessels, but as it is difficult to secure a perfectly uniform flow, free from eddies, in very large vessels and as a very much longer time is required in order to effect the separation of larger quantities of materials, it is usually necessary to work with only a very small quantity of the material, preferably that which has previously been passed through a No. 200 sieve. As a matter of convenience, it is usually assumed that all the "true clay" in a material (except in the case of indurated clays and some

shales) will be removed by a stream of water flowing at the rate of 0·43 inch per minute or 0·18 mm. per second. Such a stream was found by Seger to remove all particles with a diameter of less than 0·0004 inch or 0·010 mm., so that it washes out all the clay. The "clay" so removed is usually contaminated with a variable proportion of rock dust and other non-plastic material and, in some cases, it may be quite devoid of "true clay."

A typical elutriator (fig. 4) consists of a glass vessel about 60 cm. high, the upper 10 cms. (*D* to *E*) being cylindrical and about 5 cm. internal diameter, and the lower part (*E* to *F*) conical and tapering from 5 cm. internal diameter to 5 mm. diameter. The lower end is connected to a tube *G*, 5 mm. in diameter, through which the water or other elutriating fluid enters and flows upward through the apparatus. This narrow portion is necessary to ensure a truly central flow, which is quite free from eddies and side currents. The top of the elutriator is constricted so as to hold a rubber stopper carrying the overflow-tube *A*, which also acts as a manometer and enables the velocity of the liquid to be measured at any moment. At *B* in this tube is a small hole, 1·5 mm. in diameter, the edges of which have been rounded by fusion so as to provide a smooth aperture.

Fig. 4. — Schoene's Elutriator.

The pressure tube *I* should be made of barometer tubing, and should be carefully tested to see that it is really uniform. The bends at *A* and *B* must be very carefully made, so that no narrowing of the internal bore occurs. The upper vertical part of the tube is about 1 metre long and should be divided into cm., and the lowest ten of these divisions should be subdivided into mm. The end *H* is connected to a water tank, or, preferably, to a large Marriott bottle, so as to maintain the water at a constant rate of flow, the volume of water being regulated with a small pinch-cock. A small piece of wire gauze is fitted into the bottom of the conical portion at *F*, by means of a perforated cork, in order to prevent any coarse particles from becoming stranded in the bend *C*.

The stopper and pressure-tube are removed and the vessel is filled to the middle of the cylindrical portion with water, and the water is allowed to flow at the prearranged rate. A weighed quantity of the material to be examined (*e.g.* 10 grams) is then placed in the vessel. If necessary, it may be transferred by the aid of a little water. The pressure-tube is rapidly inserted and a large pan placed ready to receive the overflow. The supply of water is continued until no further particles are carried away in suspension, after which the apparatus is dismantled, the residual matter is carefully removed, collected in a small basin, dried and weighed as "silt." It is not

usual to attempt to dry and weigh the " clay " portion, unless this is required for some other purpose.

The elutriator should be carefully calibrated before use and the height of the water in the pressure-tube, which corresponds to the required velocity, should be ascertained. The area of the cylindrical portion D, E is ascertained by filling the apparatus with water exactly to the level E, and then running in water from a burette or from a weighed vessel until it is exactly at the point D; the volume in c.c. or weight in grams of the water so added, divided by the height h in cm., gives the area (a) of the apparatus at the point of minimum velocity. To ascertain the rate of flow, the apparatus is set to work without any solid material and the quantity of water flowing through it in a period of exactly sixty seconds is measured or weighed, the height of the water in the pressure-tube being carefully noted. The weight or volume of the effluent water divided by the area (a), and by 60, gives the rate of flow in cm. per second. If it is either faster or slower than is required, the pinch-cock which controls it must be adjusted and another trial made. After the correct rate has been obtained, it is only necessary to note the height of water in the pressure-tube and to maintain the water at this height throughout all future tests with the same apparatus.

If the same vessel is to be used for separating particles of different sizes, a record of the height of the water in the pressure-tube corresponding to such sizes should be kept. Various other patterns of elutriator are in use, but the general principle is the same in all.

Krehbiel's elutriating apparatus consists of a number of metal containers, consisting of a hollow cylinder surmounting an inverted hollow cone. Each container has a different diameter, so that the speed of the water flowing upward through it effects the suspension of particles of different sizes. By this means a good separation can be effected, though a long time and a very large volume of water are required.

A small elutriator, of the same type, originally devised by Schloesing, but modified by Lowry, to ensure more rapid working, consists of a long, conical-shaped vessel (fig. 5) mounted on a heavy foot. A loose-fitting brass cap lying on the top serves to carry a long glass tube, the lower end of which reaches to within an inch or two of the bottom of the vessel. The upper end of the tube projects into the " constant level " apparatus by means of which a constant pressure or head of water is maintained.

The apparatus is put into operation by allowing water to flow from any convenient tap or other source of supply, T, into the constant level tube, A. This fills up and the water flows down the central glass tube into the elutriator, which gradually fills and overflows into a graduated glass cylinder placed alongside. The rate of flow of the water through the elutriator is controlled by the size of the orifice of the long central tube. By means of a number of tubes, each having a definite sized orifice, it is possible to regulate the flow as required.

The elutriation test is made by weighing 10 or 20 grams of the dried material, working it up with water in a mortar to a thin creamy paste, and washing it into the elutriator.

A tube of slow rate of flow (*e.g.* 30 c.c. per min.) is placed in position and the water turned on. The material is agitated and a certain quantity overflows with the water into the graduated cylinder. When the water becomes clear, owing to the removal of the lightest particles by the water, the apparatus is stopped, the graduated cylinder is changed and another tube of more rapid flow is inserted. This process is repeated with one tube after another, each lot of overflow water being put aside so that the clay, etc., in it may settle.

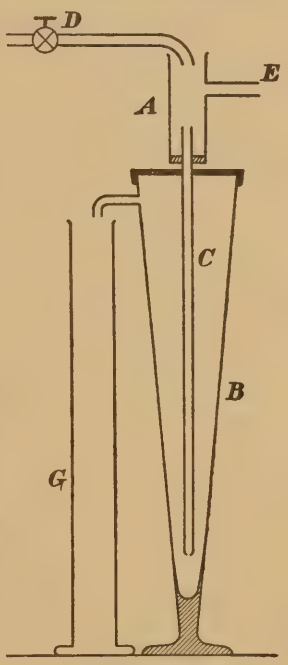


Fig. 5.—Lowry's Elutriator.

The supernatant clear liquor is carefully poured off and the material washed out into small beakers, allowed to settle a second time, and finally it is transferred, after pouring off the clear water, to weighed watch-glasses, dried at 110° C., and the net weight of material in each portion is weighed. In this way, the original sample is graded into as many grades as there are tubes corresponding to various rates of flow.

The apparatus must be standardised by testing materials of known fineness so as to determine the range of particles washed out by particular velocities.

Of these various types of elutriators, Schoene's (fig. 4) is usually the most accurate, Schloesing's (fig. 5) the most rapid and Krehbiel's the most suitable for larger quantities or for separating the finer particles into several grades.

Air separation may be described as elutriation by air instead of by water and is effected in a similar manner. The chief difficulty lies in securing a current of air at a sufficiently uniform velocity. When this is available, air separation has the advantage of enabling much finer particles to be separated than is possible when water is used.

Sedimentation.—Instead of removing some of the particles by a current of water or air as just described, it is sometimes more convenient to suspend all the particles in water and then to leave them for some prearranged time. Most of the larger or denser particles will then settle ; particles still remaining in suspension may be removed by pouring off the liquid. If the treatment with water is repeated, the periods of quiescence being increased progressively, a series of different "grades" will be produced.

The rate at which the various particles will settle may be calculated by means of Stokes' law :—

$$V=\frac{2(D-d)}{9y}gr^2$$

or

$$V=Cr^2 \text{ when } C=\frac{2(D-d)g}{9y}$$

where V=the velocity of the particles in cm. per sec.
y=the viscosity of the liquid.
r=the radius of the particles in cm.
g=981.
d=the specific gravity of the liquid.
D=the specific gravity of the particles.

Table IV shows the time taken by particles of clay, silica, and other materials of specific gravity 2·6 to fall through the distance mentioned in the last column of the table :—

TABLE IV.—*Settling of Particles in Water.*

Size of Particles.		Time of Settling.	Depth from Surface.	
mm.	inch.		mm.	inch.
0·1	0·004	20 sec.	140	5·6
0·05	0·002	1 min.	120	4·8
0·01	0·0004	10 min.	90	3·6

This formula assumes that (*a*) the particles of solid matter are much larger than the particles of liquid ; (*b*) the liquid is of infinite extent in comparison with the sinking particles ; (*c*) the particles are smooth and rigid ; (*d*) no slipping occurs between the particles and the liquid ; (*e*) the velocity is small ; and (*f*) the particles are small, but not excessively so. E. Cunningham has shown that, to make this law applicable to the smallest particles, it must be multiplied by $\left(1+\frac{A}{r}\right)$, where A is " a constant depending on the collisions between the gaseous molecules and the solid particles." It lies between 0·81 and 1·63. The finest possible colloidal particles may remain suspended indefinitely on account of Brownian movement.

When the velocity of sinking is great, this formula is inapplicable, but for all grains of less than 200-mesh (other than flat flakes, see p. 50), it is sufficiently correct.

Sedimentation tests may very conveniently be carried out in cylindrical vessels about 6 inches high, the most suitable diameter depending on the quantity of material used. In order to avoid errors due to irregular movement of the particles in a concentrated suspension, the quantity of water in any vessel should never be less than 20 times the weight of the solid material. If the materials are such as correspond to Table IV, the following procedure is convenient : the material is stirred thoroughly with at least 20 times its weight of water until every particle is separated from its neighbours and is then allowed to stand [1] 10 minutes, after which the uppermost

[1] The total depth of the water should be about 6 inches.

3·6 inches of the liquid is carefully siphoned or poured off, care being taken not to disturb the material at a greater depth. The liquid so removed is assumed to contain all the particles smaller than 0·01 mm. (or 0·0004 inch), and the residue to contain all the larger particles. The vessel is refilled, its contents are again thoroughly stirred and then allowed to settle for 1 minute, after which 4·8 inches of liquid are drawn off, the residue is assumed to contain only particles more than 0·5 mm. (or 0·002 inch) in diameter and the decanted liquid to contain those between 0·01 and 0·05 mm. diameter (or 0·0004 and 0·002 inch).

Some people prefer to repeat each period of settling twice or three times, with the idea of effecting a cleaner separation. This is especially necessary with some plastic clays, which are very difficult to treat satisfactorily by this process.

The fact must not be overlooked that the Stokes formula, whilst quite applicable to non-plastic materials, is less satisfactory when applied to plastic ones, and particularly to semi-flocculated clays. The aggregations of plastic clay particles are so voluminous and their specific gravity is so close to that of water, that they do not settle out at a normal rate and they are so highly absorbent that small particles of fine sand and silt tend to adhere to them and are carried along with the clay. Hence, this method often shows too high a proportion of " clay " and correspondingly low proportions of the coarser materials. Conversely, some of the clay also tends to adhere to the sand and silt and thus gives slightly inaccurate results. For these reasons, where much plastic clay is present, it is very important to have the material thoroughly disintegrated and to repeat each period of settlement several times, so as to ensure as sharp a separation as possible. Owing to the greater distance they have to travel, clayey materials are often more accurately and sharply separated by elutriation.

An ingenious modification of the sedimentation method just described has been devised by H. G. Schurecht,[1] who claims that it yields very accurate results with either plastic or non-plastic materials and is much more accurate than elutriation or ordinary sedimentation in determining the proportion of particles of various sizes. In Schurecht's method the material is suspended in water, as before, and is transferred to a glass cylinder 15·5 cm. high and 3·5 cm. internal diameter, the mixture occupying a depth of exactly 12·7 cm., when a glass plummet is suspended in it from the arm of a balance by a thin copper or gold thread. The plummet, which should just be covered by the liquid, is then weighed at intervals of 1, 2, 3, 5, 10, 20, 35, and 60 minutes, 2, 3, 5, and 7 hours, and 1, 2, 3, 5, 10, 15, 20, and 30 days, or at such other intervals as may be desired. When the liquid is to be allowed to stand for several days, the plummet may be removed and the glass cylinder tightly closed, but its contents must be disturbed as little as possible when the plummet is again immersed. From the weighings, it is possible to determine the average weight of suspended matter in that portion of the slip in which the plummet is immersed, from the equation $W=\frac{D(S-d)}{D-d}$ where W is the average weight per c.c. of slip, D is the specific gravity of the material, d that of the water, and S that of the slip. The

[1] *J. Amer. Cer. Soc.*, **4**, 812 (1921).

resulting figures show the weight of material which settles in different periods of time and from this may be calculated the proportions of particles of different sizes.

Comparison of Different Textures.—One of the most obvious means of comparing different textures is to compare photomicrographs of the various specimens, but this method is far from accurate. It is the only one available in many instances, but where the material can be disintegrated without crushing any of the component grains, a much more accurate comparison is possible. For instance, the proportions of grains of different sizes in each material may be compared, though this is tedious and not always very enlightening and many people would prefer to use one figure to express the fineness or texture. One of the most convenient means for so doing was devised by W. Jackson and was termed by him the *surface factor*. Jackson accepted the figures for the average diameters of the grains in the four divisions given in Seger's classification of the clays (p. 35) and, assuming the particles to be true spheres, he calculated the average surface area of the materials in each of the four divisions and obtained the results shown in Table V.

TABLE V.—*Surface Factors*

Material.	Clay.	Silt.	Dust Sand.	Fine Sand.
Average diameter of grains, mm. .	0·005	0·0175	0·0325	0·080
Average surface area of equal weights of grains . . .	3367	962	518	91

The same method of calculation may be extended to larger particles which yield the following factors :—

Passing through	30-mesh,	average	diameter	0·4	mm.	Factor	45
,,	,,	25	,,	,,	,,	0·5	,,	,,	36
,,	,,	12	,,	,,	,,	1·0	,,	,,	23
,,	,,	5	,,	,,	,,	2·5	,,	,,	9

but these figures are not so accurate as those for smaller grains.

From these figures it is possible to obtain a " fineness figure " or " surface factor " for each material by multiplying the percentage weight of each grade of material present by the average surface area of the grains in that grade, adding the products so obtained and dividing the result by 100. This figure for the " surface factor " is not strictly accurate, but it is sufficiently so for comparative purposes.

A modified method of calculation suggested by Purdy is intended to give a more nearly correct result. Purdy divides 1 by the various average diameters and thus

obtained the figures 200·00, 57·14, 30·97, and 12·50, which are treated in the same manner as by Jackson, but the resultant surface factor figure is smaller and Purdy regards it as rather more accurate.

J. W. Mellor has shown that the true average diameter of a series of particles of different sizes is not the arithmetic mean of the largest and smallest diameters, but corresponds to

$$\sqrt[3]{\frac{(D+d)(D^2+d^2)}{4}},$$

where D is the diameter of the largest and d that of the smallest particles in each group. By using this formula and dividing clays and allied materials into three divisions, namely, (*a*) particles below 0·010 mm. diameter, (*b*) those between 0·01 and 0·063 mm. diameter, and (*c*) those from 0·063 to 0·107 mm. diameter, he obtained the following factors, 359, 53·9, and 26·0, which, when multiplied by the respective weights of the different grades, and added together, give possibly the most accurate value attainable of the average surface area of the material.[1] No surface factor is entirely accurate for the following reasons, given by Heath and Green [2] :—

(i) The particles are not wholly spherical, though their sphericity has been assumed in determining the surface factor.

(ii) The specific gravities of all the particles are not the same, though a constant specific gravity is assumed.

(iii) The conception of an "average diameter" is an inadequate approximation. The method has, however, many conveniences and is very useful.

Another method of comparing the texture or fineness of various materials is that recommended by the American Foundryman's Association, which consists in multiplying the percentage by weight of material passed through each sieve by the mesh number of that sieve, adding the results obtained and dividing by 100. This method is satisfactory for most purposes, though not so accurate as those mentioned above.

Various attempts have been made to compare various textures by plotting the results of sieving or similar tests in the form of a graph, using the horizontal scale for the size of grains and the vertical scale for the percentage of grains of each size. This method is convenient in comparing mixtures to secure a maximum density (see also p. 33). It has been modified by Boswell, who prefers to plot the sizes of the grains on a horizontal logarithmic scale and the cumulative percentage of the various sizes on a plain vertical scale, as in fig. 6. In Boswell's method the scale of sizes is extended in a convenient manner, and a mixture consisting of particles entirely of one size is represented by a vertical line as at A, B, instead of by a single point. For particles of various sizes, the more nearly vertical the line, the more nearly uniform is the grading. As small variations in the sizes of the grains causes large deviations from the vertical, this method provides a very accurate means of comparison within a very small space.

Another method is that of M. Feret, who recognises only three groups of particles ;

[1] See also Perrot and Kinney, *J. Amer. Cer. Soc.*, **6**, 417 (1923); *Bull. Amer. Cer. Soc.*, **2**, 121 (1923).

[2] *Handbook of Ceramic Calculations*, p. 160.

G=particles of 5 mm.–2 mm. diameter, M=particles 2 mm.–0·5 mm., and F=particles less than 0·5 mm.; he represents the proportions of material of each of these sizes

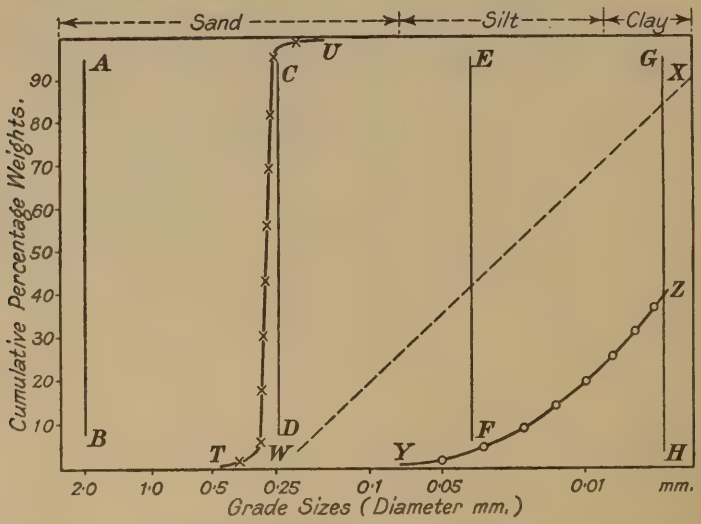


FIG. 6.—BOSWELL'S GRADING GRAPH.

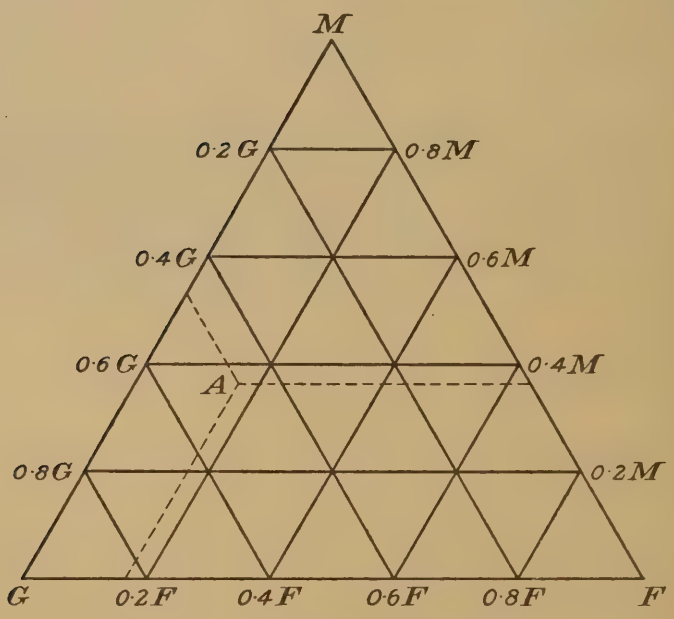


FIG. 7.—FERET'S TRIANGULAR DIAGRAM.

by a single point on a triangular diagram (fig. 7), this point being at the intersection of lines drawn from each side from the points expressing the proportion of each size

of grains, the lines being drawn parallel to each side as shown. Each of the points, G, M, and F, represents a mixture consisting wholly of those particular sizes of grains and A one containing 47 per cent. of G, 16 per cent. of F, and 36 per cent. of M.

Homogeneity

For most purposes for which ceramic materials are used it is not only important to have a suitable texture, but also that the texture should be uniform throughout the entire mass. Thus, if a considerable number of large particles are present they should not be segregated, but distributed uniformly through the material. In some articles, such as building bricks, homogeneity is not so important, though very desirable, but in refractory articles it is almost essential, because a material which is not homogeneous is very liable to crack or spall. Homogeneity is especially important in crucibles, retorts, glass-melting pots, pottery, porcelain, etc., and for this reason special care is required in preparing the clay to be used for such articles. Large and thick blocks must also be made as homogeneous as possible, on account of their liability to develop internal stresses.

Homogeneity in raw materials is obtained by (*a*) constancy in the physical and chemical composition of the material; (*b*) thorough mixing; and (*c*) uniform distribution of moisture.

Constancy in composition is attained chiefly by the proper choice of materials, the rejection of irregular material and, to some extent, by reducing the larger particles to a sufficiently small size by means of crushing or grinding machinery. Thorough mixing is largely a matter of time and the use of a suitable form of mixer. The uniform distribution of moisture is also obtained by thorough mixing and, in the case of mixtures containing clay, by allowing them to stand in a moist condition for a considerable time, so that the moisture passes through the pores of the material and uniformly permeates the whole mass. This process, known as "Souring," is fully described in Chapter VI.

The principal methods of producing a homogeneous mass from the materials used in the ceramic industries are (*a*) treading, (*b*) wedging, (*c*) mixing with spades, (*d*) pugging, (*e*) tempering, and (*f*) blunging. They all require the materials to have previously been crushed or ground to particles of suitable size.

Treading is one of the most effective methods for thoroughly mixing fine plastic materials where a specially homogeneous structure is required, but it is by no means pleasant and is very costly. The mass is placed on a concrete floor, moistened and then roughly mixed with spades. It is then spread out and trodden by men with bare feet, the clay being squeezed between the toes and so thoroughly mixed. Several treadings, alternating with spade-mixing, are sometimes employed to secure an effectively mixed paste. Treading is chiefly employed in the manufacture of crucibles and glass-house pots.

Wedging consists in cutting a plastic paste into pieces and throwing them together again, the mass being turned and the cutting and throwing actions being repeated until the mass is homogeneous. This method is very effective, but is slow and tedious, so that it is chiefly used in preparing the paste for making pottery,

china ware, porcelain, crucibles, etc. and for thoroughly mixing small quantities of material.

Spade-mixing is sometimes useful as a preliminary treatment, so as roughly to mix the materials together before using one of the other methods. The first mixing of dolomite mixtures is usually done with spades and in the manufacture of crucibles and glass-house pots the materials are turned over with spades before treading or pugging them. Materials containing coke and tar are sometimes mixed wholly by means of spades.

Pugging consists in passing the material and a suitable amount of water through a trough containing one or more shafts fitted with rotating blades which cut and churn the material and at the same time drive it forward to the exit end of the machine. If a cylindrical pug-mill is used the resultant paste will be extruded in the form of a long column, which may be cut up into pieces of suitable size for moulding, etc., but when an open trough mixer is used the resultant material has no definite shape. Pugging produces a fairly homogeneous structure, but it is the least satisfactory of mechanical mixers, and is only used for work where a completely homogeneous structure is not required, or would cost too much to produce. It introduces air bubbles into the clay-paste ; these may produce too porous a mass, or they may cause other troubles at a later stage of manufacture or when the articles are in use. Pug-mills are largely used for mixing materials for the manufacture of bricks, tiles, terra-cotta, pottery, and similar articles, and in the manufacture of some refractory bricks and blocks made of fireclay, magnesia, bauxite, etc.

Tempering is a term which is sometimes applied to any process of mixing in which a paste is produced, but it is often restricted to the use of an edge-runner mill which produces a much more homogeneous mass than a pug-mill, though at a greater cost. The material to be tempered is placed in a circular pan and is rubbed together and thoroughly mixed by two or more rollers which rotate in the pan. As a rule, 15–20 minutes' treatment in a mill of this kind will produce a sufficiently homogeneous mass, but for crucibles 30 minutes' treatment is better and for some special work several hours may be necessary. Edge-runner mills are used for tempering clay, etc., in the manufacture of paste for some of the better quality of terra-cotta, refractory cements, and sometimes for magnesia and bauxite bricks. They are almost invariably employed for preparing the materials used in making silica bricks.

Blunging consists in mixing the materials with water in a tank so as to form a cream or slip. The mixing, or, more correctly, stirring, is usually effected by a number of arms on a vertical revolving shaft, and if the solid particles are not too large it produces a very homogeneous mixture. This method is specially useful for preparing the material used for fine pottery, china ware, and porcelain, as well as for casting, glazes, etc.

The aim of all these methods of preparation is that a perfectly structureless material of absolutely even composition may be produced. Defective mixing, whereby complete homogeneity is not obtained, usually results in defective goods, and it has been proved repeatedly that if the mixture be imperfect no later treatment can possibly remedy defects in the earlier stages of manufacture.

It is only by paying full attention to the preparation of the paste or slip that irregular behaviour can be avoided and losses prevented and, in some cases, this is far from easy. Some materials are of such a nature that it is almost impossible to grind them alone; others retain the lamellar structure in spite of their subjection to the heaviest crushing machinery, and to work such materials satisfactorily and profitably needs great skill and care.

The addition of another material, such as sand, to clay will often facilitate the working of a mixture and render the composition of the mass more homogeneous. This is particularly the case with "fat" or "scurfy" clays, which adhere so tenaciously to the machinery when worked alone, that no progress with them is possible. Flaky or "scurfy" clays from an ancient river-bed are amongst the most troublesome of clays to render homogeneous and their treatment requires much patience and time, as well as skill. The result is that they prove very costly as a raw material and should, when possible, be abandoned in favour of a more easily worked deposit, unless only the commonest class of goods are being manufactured.

In some cases the texture need not be homogeneous; for instance, some firebricks and other articles are required to be porous internally and to have a dense surface. The former makes the articles sufficiently resistant to sudden changes in temperature, whilst the dense exterior has a great resistance to the corrosive action of flue gases, etc., and to abrasion.

Porosity

The porosity of a material is the total proportion of the voids or interstices to the solid particles of which it is composed. These voids are usually filled with air. It should not be confused with permeability, for although the porosity of a mass is directly proportional to the fineness of its particles, its permeability depends on their position and shape. Many clayworkers habitually use the term "porosity" when they really mean permeability. A proof that, contrary to the usual opinion, strong clays are more porous than sandy ones is to be found in the fact that they need more water of manufacture to make them sufficiently plastic for moulding.

When sand or other coarser materials than the clay-particles are added to a clay, the porosity of the latter is diminished and its permeability is increased, the porosity being least and the permeability greatest when the material is entirely composed of large irregular pieces which do not fit well together.

According to E. W. Washburn,[1] there are six types of pores: (*a*) closed pores, (*b*) channel pores connecting separate pores, (*c*) blind-alley pores, (*d*) loop pores, (*e*) pocket pores with narrow necks, and (*f*) micropores, which are so small as not to be filled with water or other liquid in any ordinary period of soaking. These different kinds of pores produce two sets of results when the porosity of a material is determined, viz. (*a*) the true porosity, and (*b*) the apparent porosity.

The **true porosity** is the relation between the volume of the article and the total volume of water absorbed by the pores when the article is soaked in water, plus the volume of the pores which are sealed by vitrified matter and so are not

[1] *J. Amer. Cer. Soc.*, **4**, 918 (1921).

filled in the ordinary way. It is difficult to determine the total porosity accurately, but fortunately it is not usually of much importance. It is usually calculated as shown on p. 83.

The **apparent porosity** is the relation between the volume or weight of an article and the volume or weight of the water or other liquid absorbed when the article is immersed in it. This figure is the one generally used as a measure of the porosity, and unless otherwise stated it is usually understood that figures relating to the porosity indicate the apparent and not the true porosity. The apparent porosity is determined as shown on p. 81.

Both the true and the apparent porosity may be expressed as (*a*) percentage by weight, and (*b*) percentage by volume. The percentage of porosity by weight shows the weight of water absorbed by 100 units of weight, whilst the percentage of porosity by volume is the volume of water absorbed in 100 volumes of the material or article. For many years it has been customary to use the former and express the porosity in terms of the weight of the water absorbed, but the method of expressing it by volume has the advantage of indicating the volume of the pores. The volume of articles of simple shape may be calculated from direct measurement of the dimensions, but where the shape is complex the volume must be determined by finding the difference between the weight in water and the weight in air. This, if gram weights are used, gives the volume in c.c., or if in ounces, when multiplied by 1·734, gives the volume in cubic inches.

The expression of porosity by weight is also complicated by the fact that all materials have not the same density, *e.g.* clay articles may have a density of 1·4 to 2·6, so that the porosity results on different samples cannot be compared accurately. The expression of porosity wholly in terms of volume is, therefore, the most satisfactory.

The porosity of various materials may be influenced by some or all of the following : (*a*) the shape of the particles, (*b*) the size of the particles, (*c*) the grading of the particles (if any), (*d*) the nature of the materials comprising the mixture, (*e*) the treatment to which the materials are subjected during manufacture, and (*f*) the relative position of the particles, *i.e.* whether they are closely compacted or lie loosely on one another.

The effect of the shape, size, and grading of the particles has been considered on pp. 27–44 in connection with *Texture*, but it should also be borne in mind that rounded grains produce a more porous mass than angular ones when pressure is employed to shape the articles. When no pressure is applied, rounded grains may sometimes give a smaller porosity (p. 28). The porosity of mixtures consisting of perfect spheres of uniform size gives some idea of the porosities which may be obtained with round-grained materials. When one sphere rests on another the volume of the voids is 47·6 per cent. of the volume of the mass ; when each sphere rests on two others it is 39·5 per cent. ; whilst when each sphere rests on three others, *i.e.* in a state of the closest possible packing, the porosity is 25·95 per cent. These results are not obtained with ordinary minerals, as they are not perfect spheres, but they have a fairly definite relation to the results obtained with clays, etc. Thus, it has been found that for all particles up to $\frac{1}{4}$ inch diameter the percentage of voids is

practically constant, provided all the particles are of the same size. Thus, a material consisting of grains of about 40-mesh will have the same porosity as one consisting entirely of grains of about 10-mesh.

Mixtures of fine materials have a large surface factor and are usually more porous in the raw state than those containing coarse materials, as is shown in Table VI,

TABLE VI.—*Relation of Porosity to Texture*

Average Fineness (Purdy's Factor).	Pore Space.	Average Fineness (Purdy's Factor).	Pore Space.
	Per cent.		Per cent.
174	43·45	88	38·00
163	44·70	70	32·91
131	40·43	63	39·52
103	43·20	54	38·83

due to Ries, comparing the fineness and porosity of sands. J. S. M'Dowell [1] found that the minimum porosity in silica bricks is obtained by using grains of medium fineness, and the maximum porosity by the use of coarse grains as shown in Table VII.

TABLE VII.—*Texture and Porosity of Silica Bricks*

Kind of Brick.	Texture (per cent. passing through Sieves).						Temperature of burning, Cone.	Open Pore Space, per cent. of Volume.	Mean Pore Space.
	8.	16.	20.	30.	40.	40–.			
Coarse. .	15·3	13·4	4·6	5·4	4·8	56·5	15	25·7	26·8
							15	26·5	
							14	28·5	
							13	25·7	
Medium .	10·2	13·1	2·2	5·0	4·7	64·8	15	21·3	21·2
							15	22·3	
							14	22·7	
							13	19·2	
Fine . .	..	14·3	4·1	6·5	4·1	71·0	15	22·7	22·5
							15	22·3	
							14	23·2	
							13	21·7	

[1] Bull. 119, *Amer. Inst. Min. Eng.*

Table VIII is due to M. Phillipon,[1] who investigated the effect of the size of the grains on the porosity of silica bricks made of four types of quartz having the following fineness :—

	Per cent. passing a 200-mesh Sieve.	Per cent. of Particles between 2 and 8 mm. diam.
A . .	60	40
B . .	50	50
C . .	40	60
D . .	30	70

The porosities were as follows :—

TABLE VIII.—*Porosity of Silica Bricks*

Material.	Porosity.	Material.	Porosity.
Quartz 1, A	18·0	Quartz 3, A	21·0
,, B	18·6	,, B	19·8
,, C	17·7	,, C	19·0
,, D	16·2	,, D	18·2
Quartz 2, A	22·0	Quartz 4, A	20·5
,, B	19·3	,, B	19·7
,, C	18·5	,, C	17·8
,, D	17·0	,, D	15·9

Any increase of porosity produced by fine grains can only occur at temperatures below that at which vitrification commences and the pores begin to fill with fused material. Thus, in some fine-grained clays it was found that the porosity was highest with materials up to 1180° C.; between 1180° C. and 1300° C. there was little difference in the porosity, but at temperatures over 1430° C. the porosity is reduced almost to nil, as a result of vitrification. Hence, whilst fine grains are a cause of high porosity in the unfired material, in articles fired at high temperatures, fine grains are a cause of smaller porosity than coarser ones, as the latter are not so easily fused and consequently their interstices are not filled with vitrified matter.

Grading (p. 31) has a very important effect in reducing the porosity of a material, and where high porosity is required, as in moulding sands used for casting molten metal, the grains should be as uniform as possible in size, so as to enable the gases evolved during the casting process ample opportunity to escape. The use of very small grains in a moulding sand is undesirable, as they occupy the interstices between the large grains and, by reducing the porosity, they prevent the gases from escaping.

Sometimes, apparently, widely differing mixtures of grains of different sizes give

[1] *Rev. de Métal.*, **15**, 51 (1918).

satisfactory results ; when this is the case it will usually be found that the porosities are very similar. Thus, Dauphin found the two following mixtures gave satisfactory results when made into silica bricks :—

A. Seventy per cent. residue on 9-mesh sieve ; 30 per cent. on 20-mesh sieve. Porosity, 40 per cent.

B. Forty-seven per cent. residue on 9-mesh sieve ; 28 per cent. on 20-mesh sieve ; 3 per cent. residue on 50-mesh sieve ; 22 per cent. on 200-mesh sieve. Porosity, 46·4.

It will be seen that, whilst the proportions of grains of various sizes are widely different, the difference in the porosity is quite small.

The porosity of a dry mass depends largely on the pressure applied to it in packing, moulding, etc. Table IX, due to Foster and Emery,[1] shows the effect of pressure on clay grains which have passed through a 10-mesh sieve.

TABLE IX.—*Effect of Pressure on Porosity of Clay*

	Pressure.	Porosity.		Pressure.	Porosity.
	Lbs. per square inch.	Per cent.		Lbs. per square inch.	Per cent.
A	500	38·71	J	2750	26·31
B	750	34·73	K	3000	25·58
C	1000	32·59	L	3250	25·70
D	1250	30·83	M	3500	24·94
E	1500	30·65	N	3750	24·90
F	1750	30·83	O	4000	24·13
G	2000	28·38	P	4000 and 4 bumps	22·83
H	2250	27·47	Q	4000 and 6 ,,	22·41
I	2500	26·87			

Other conditions being equal, hand-moulded bricks made of a soft plastic paste will be more porous than if made of a stiffer paste, as in the stiff-plastic process, on account of the larger amount of water and the smaller pressure used in making them from a soft paste.

The nature of the materials comprising the mass has a very important influence on its porosity, especially in the fired state, because of the chemical reactions which take place in the firing and of the partial fusion which occurs. Similarly, when some materials, such as chalk, are in association with clay, the compound silicates which form when the mixture is heated to bright redness tend to fuse and reduce the porosity of the mass.

Materials Increasing the Porosity.—If carbonaceous matter, such as sawdust, is added, as in the manufacture of light, porous bricks, the porosity before firing will be slightly reduced ; but when the mass is fired, the carbonaceous matter burns away, leaving corresponding pore-spaces, so that the porosity of the fired mass is roughly

[1] *Trans. Eng. Cer. Soc.*, **15**, 143 (1915–16).

proportional to the volume of carbonaceous matter added and is, in some cases, very high. The chief combustible materials added to clays, etc., to increase their porosity are hardwood sawdust, cork, seeds, naphthalene and, occasionally, finely ground coke. The maximum proportion which can be added depends on the binding power of the other ingredients. The porosity of a mass may also be increased by the addition of a porous material, such as grog (p. 36) or kieselguhr (p. 7). Grog is sometimes added to fireclays to increase the porosity of the product, the increase in porosity being roughly proportional to the grog added unless the grog is very fine, when the porosity is not increased to the same extent, because some of the fine particles may fuse and close some of the pores and thus reduce the porosity.

Highly porous articles, such as insulating bricks and filter "candles," are sometimes made by mixing kieselguhr with a small proportion of highly plastic clay and burning at a moderate temperature. Such articles depend for their porosity on that of the kieselguhr used.

Materials Reducing Porosity.—The materials which cause a reduction in the porosity of fired articles partly composed of clay are either fusible at the temperature at which the article is fired, or they are *fluxes* which combine with some of the other constituents and form a fusible glassy mass, which fills the pores of the material. The most active flux in this respect is lime ; when this is added to a clay or siliceous mixture, the reduction in porosity commences at about 900° C. ; magnesia is rather less powerful and felspar does not commence to reduce the porosity until a temperature of about 1200° C. is reached. The effect of felspar on the porosity of burned china clay is shown in Table X, modified from one by A. Heath.

TABLE X.—*Effect of Heat on Mixtures of China Clay and Felspar fired at Cone* 9 (1280° *C.*).

Felspar.	Porosity.	Felspar.	Porosity.	Felspar.	Porosity.
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
..	22·500	35·0	0·260	67·5	0·370
2·5	19·390	37·5	0·390	70·0	0·125
5·0	17·132	40·0	0·458	72·5	0·267
7·5	14·871	42·5	0·315	75·0	0·264
10·0	11·857	45·0	0·368	77·5	0·176
12·5	10·386	47·5	0·780	80·0	0·263
15·0	9·536	50·0	0·356	82·5	0·300
17·5	6·003	52·5	0·416	85·0	0·404
20·0	4·522	55·0	0·287	87·5	0·409
22·5	2·081	57·5	0·310	90·0	0·368
25·0	0·463	60·0	0·290	92·5	0·281
27·5	0·433	62·5	0·308	95·0	0·181
30·0	0·344	65·0	0·341	97·5	0·293
32·5	0·283			100·0	0·265

According to tests made by Bleininger and Moore,[1] the presence of Cornish stone reduced the porosity of Florida kaolin as follows :—

TABLE XI.—*Effect of Cornish Stone on Porosity of Kaolin*

Temperature of Burning.	Cornish Stone.	Porosity.
Cone.	Per cent.	Per cent.
01	15	38
	40	30
	60	21
	80	5
11	15	26
	30	12·5
	50	1

The size of the particles of any fluxes present also has a marked effect, as shown in Table XII, due to J. Keele,[2] which gives the effect of the fineness of felspar on the porosity of felspar-kaolin mixtures.

TABLE XII.—*Effect of Fineness of Fluxes on Porosity*

Size of Particles of Felspar.	Felspar.	In dry State.	Temperature of Firing in Seger Cones.						
			05.	1.	3.	5.	7.	9.	12.
	Per cent.								
40-mesh	40	31·00	34·50	31·70	27·55	23·65	19·60	10·95	4·960
	30	33·63	37·30	30·95	28·55	25·40	21·70	14·40	9·330
	20	36·60	40·00	37·15	32·00	30·00	25·40	18·45	14·21
	10	39·50	43·00	40·00	35·70	32·35	30·50	23·00	18·65
100-mesh	40	32·85	36·50	30·80	23·80	17·10	13·20	6·60	1·40
	30	35·20	39·00	38·30	29·40	25·05	18·30	10·80	4·92
	20	37·00	41·00	38·40	30·60	27·50	27·10	14·40	8·87
	10	39·20	42·70	38·15	34·55	32·25	25·30	23·95	16·37
200-mesh	40	35·10	38·60	22·65	18·50	14·80	6·00	..	..
	30	36·45	40·00	28·80	20·50	15·80	13·65	4·40	..
	20	38·05	41·55	33·60	28·45	23·70	21·90	10·50	7·11
	10	41·10	43·80	36·70	33·15	28·25	27·08	17·20	12·75

[1] *Trans. Amer. Cer. Soc.*, **10**, 313 (1908). [2] *Ibid.*, **13**, 731 (1911).

It will be seen that the finer the flux, the more the body is vitrified and the lower the porosity.

According to H. G. Schurecht,[1] the addition of electrolytes to a clay influences its porosity when the clay is in the dry state, alkalies reducing the porosity and calcium hydroxide increasing it. Acids in small quantities increase the porosity in the dry state, but larger quantities of acid reduce it.

The effect of various bonds on the porosity of silica bricks, after firing at various temperatures, is shown in Table XIII, due to Scott.[2]

TABLE XIII.—*Effect of Bonds on Porosity (Scott)*

Bond.	Material fired at—			
	Cone 8.	Cone 14.	Cone 16.	Cone 19.
Lime	31·8	30·0	29·3	30·2
Magnesia	30·8	31·4	30·2	30·8
Alumina	33·1	33·8	..	34·0
Ferric oxide	31·2	30·0	30·4	29·8
,, ,, and carbon	34·0	32·0	32·2	32·9
Titanium oxide	31·6	..	32·5	32·7
Lime and Magnesia	33·3	34·5	34·2	33·7
Lime and Alumina	31·8	31·6	31·2	31·0
Lime and Ferric oxide	28·4	28·0	27·4	26·5
,, ,, ,, and carbon	28·3	27·9	29·0	28·8
Lime and titanium oxide	29·2	29·5	29·9	..
Magnesia and alumina	33·2	33·4	33·2	33·4
Magnesia and ferric oxide	30·8	29·9	30·4	32·4
,, ,, ,, and carbon	31·5	31·8	..	31·9
Ferric oxide and alumina	33·0	32·5	32·4	32·2
,, ,, and carbon	32·6	33·5	33·4	32·4
Lime, ferric oxide, and titanium oxide	29·2	31·5	28·7	27·9
Fireclay	31·0	31·2	..	31·0
China clay	30·5	..	30·8	30·8

Sulphur behaves irregularly, as sometimes it makes fireclay articles slightly more porous, but more frequently it combines with any lime and alkalies in the mixtures forming sulphates and producing a denser mass.

[1] *J. Amer. Cer. Soc.*, **1**, 201 (1918).

[2] *Trans. Eng. Cer. Soc.*, **18**, 487 (1918–19).

The heat treatment to which materials are subjected also influences their porosity. Burned articles usually have a greater porosity than unfired materials up to the temperature at which vitrification commences. Articles which have been fired to higher temperatures may be less porous and in some cases are impermeable.

The " marls " used for blue bricks afford a good illustration of this ; in the dry state they are moderately porous, when fired at about 900° C. they have a porosity of about 15 per cent. by weight ; but after firing and " blueing " at about 1300° C. they absorb less than 0·1 per cent. of water.

The porosity of articles made of " clay " increases as they are heated until a temperature of about 750°–850° C. is reached. During this heating the clay shrinks and reduces the porosity, but the loss of water and carbonaceous matter, which occurs at the same time, is greater than the shrinkage, so that the porosity increases. At the moment when clay is dehydrated, the dissociation of the material and the liberation of the combined water increase the porosity to about 10 per cent. The porosity at this stage depends partly on the initial porosity of the mass and partly on the amount of carbonaceous matter present. In the manufacture of light, porous bricks, in which a large amount of carbonaceous matter has been incorporated, the porosity rapidly increases as this material burns away.

The effect of the temperature of burning on the porosity and absorption of bricks is shown in Table XIV, due to J. C. Jones.[1]

TABLE XIV.—*Effect of Burning Temperature on Porosity*

Kind of Brick.	Extent of Burning.	Pore Space.	Relative Weight of Water Absorbed.
Surface clay (plastic paste) .	Soft.	33·0	442·0
	Med. soft.	26·9	343·6
	Med. hard.	21·2	258·9
	Hard.	10·2	106·6
Shale (plastic paste) . . .	Soft.	26·2	453·1
	Med. soft.	17·8	310·1
	Med. hard.	11·6	130·4
	Hard.	5·8	48·4
Shale (wire-cut) . . .	Soft.	27·6	402·0
	Med. soft.	17·1	233·3
	Med. hard.	2·1	11·1
	Hard.	0·9	5·6

[1] *Trans. Amer. Cer. Soc.*, **9**, 578 (1907).

The influence of the temperature to which fireclays are heated on their porosity is shown in Table XV, due to E. M. Firth and W. E. S. Turner.[1]

TABLE XV.—*Effect of Burning Temperature on Porosity*

Clay.	Temperature of Burning.		Porosity Decrease.
	1400° C.	1500° C.	
Mansfield	8·0	1·4	6·6
Kilwinning	10·2	3·7	6·5
Coalbrookdale, *a*	12·5	5·7	6·8
,, *b*[2]	12·5	6·9	5·6
Ayrshire bauxitic clay	25·8	18·3	7·5
Kilmarnock	18·1	6·9	11·2
Wortley	23·3	14·1	9·2
Kilwinning aluminous shale	31·8	29·2	2·6
Huddersfield, 1	17·6	12·0	5·6
,, 2	18·8	16·4	2·4
Grossalmerode	12·8	5·4	7·4
Halifax, 1	24·9	24·1	0·8
,, 2	24·0	21·8	2·2
,, 3	19·8	10·3	9·5
,, 4	5·2	20·2	—15·0
,, 5	16·2	20·5	—4·3
,, 6	20·2	15·9	4·3
Ruabon	5·9	2·7	3·2
Armadale	13·1	3·5	9·6
Stourbridge, A	23·3	7·5	15·8
,, B	20·7	10·1	10·6
,, C	7·2	2·1	5·1
,, D	19·3	17·7	1·6
,, E	11·6	8·6	3·0
,, F	5·6	4·8	0·8
,, G *a*	18·3	12·1	6·2
,, G *b*[2]	16·5	12·1	4·4
,, H.	6·0	4·3	1·7
,, I	19·7	14·2	5·5

[1] *J. Soc. Glass Tech.*, **5**, 268 (1921).

[2] Subjected to preliminary firing at 800° C.

Further heating above 1500° C. gives a further reduction in the porosity, except in the cases of clays Halifax 4 and 5, which at 1000° C. reach the maximum temperature at which they are of value.

According to E. M. Firth, F. W. Hodkin, and W. E. S. Turner,[1] china clay has the following porosities after having been fired at different temperatures :—

TABLE XVI.—*Porosity of Kaolin*

Temperature, ° C.	Porosity.	Temperature, ° C.	Porosity.
600	51·5	1200	31·7
750	52·5	1300	14·5
900	56·2	1400	8·3
1000	52·0	1500	2·4
1100	45·6		

The proportion of sealed pores increases when articles partly or wholly made of clay are heated to a temperature above 1140° C., as vitrified matter then begins to form. This is due to the fact that a certain amount of gas is formed during the burning of the mass and, if vitrification has commenced, this gas is unable to escape and so forms sealed pores. The higher the temperature to which the mass is heated, the greater will be the proportion of sealed pores.

The changes in porosity of fireclay articles, after they have been heated several times to a high temperature, are a good criterion as to their resistance to heat. For instance, a well-burned firebrick should not show more than 5 per cent. decrease after it has been reheated to 1400° C. for two hours. The size and shape and distribution of the pores does not affect the porosity, but is important with respect to the permeability, strength, and other properties.

As a homogeneous texture is usually important, the pores of an article should be as uniform as possible. Comparatively large holes scattered throughout the mass are very undesirable and their formation should be carefully avoided by properly grading and thoroughly mixing the materials used in making the articles.

The size of the pores largely determines the rate at which water is absorbed. With very small pores the absorption is irregular ; some burned clays absorb only a small amount for several days and then suddenly absorb rapidly a further quantity of water. Usually, about 90 per cent. of the pores in an article are filled within an hour, but the remaining 10 per cent. are filled very slowly, about 9 per cent. being absorbed in the next twenty-four hours and the remaining 1 per cent. sometimes taking a week or more. The size of the pores varies according to the texture of the unfired material and with the nature of the combustible material (if any) which has

[1] *J. Soc. Glass Tech.*, **4**, 264–7 (1920).

been employed. Soft wood sawdust is undesirable, as the pores it produces are coarse and large. Hardwood sawdust is far better, as the grains are finer. Finely ground cork is excellent. Sometimes very large pores are desired and are produced by mixing seeds or grain with the clay. For most purposes, the pores should be small, not exceeding 0·01 inch diameter, as when the pores are very large the strength of the mass is reduced.

The influence of the size of the pores on the permeability is dealt with on p. 87. Porosity has an important influence upon other properties possessed by clays and other ceramic materials. Some of these are mentioned briefly in the following pages, but are dealt with fully later.

Effect of Porosity on Absorption.—The most porous articles usually absorb the greatest proportion of water or other fluid, though porosity and absorption do not bear any definite relation to each other, as the latter also depends upon other properties than the volume of pores (p. 87). The rate of absorption varies with the texture of the material. A mass composed of grains of medium size will usually absorb water more rapidly than one which contains very small pores, even though the latter has a greater porosity. All the pores are normally filled with air and it is difficult to displace this if the pores are very narrow.

Effect of Porosity on Apparent Density.—The apparent density (Chapter V) is reduced as the porosity increases, as there is a smaller volume of solid material in the total volume of the mass.

Effect of Porosity on Spalling, etc.—With few exceptions, if a fired material is porous it will not be sensitive to sudden changes in temperature, but a dense mass of the same material will spall readily. This is due to the fact that the grains in a porous mass have more freedom of movement than in a dense one, so that the stresses produced by sudden changes of temperature are immediately relieved on account of the numerous pores, without any breaking up of the structure of the mass. In time, of course, larger cracks may develop, but only very slowly if the texture of the mass is sufficiently porous. A high porosity is specially important as a means of securing resistance to sudden changes in temperature in the case of refractory materials, but less so in the case of articles which are not heated to above a dull-red heat. Sensitiveness to rapid cooling may be tested by heating a brick, or other article, to a temperature of 1350° C. for 1 hour and then subjecting it to a blast of cold air from a $\frac{3}{4}$-inch nozzle, delivering 27 cubic feet of air per minute for 15 minutes (see also Chapter XIII). Under these conditions a porous fireclay brick will not lose more than about 12 per cent. by weight as a result of spalling, whilst a dense brick may lose 65 per cent. of its weight. Silica and magnesia bricks spall to a still greater extent.

Effect of Porosity on Thermal Conductivity.—Ceramic materials of high porosity usually have a low thermal conductivity on account of the large volume of air included in them. For this reason, high porosity is undesirable where the interior of an article is to be heated by means of an exterior source of heat, though very often high porosity is essential in order that the articles may be sufficiently resistant to unavoidable changes in temperature, though it necessitates a slow rate of heating and a waste of fuel.

Where a low thermal conductivity is desirable—as for heat-insulation purposes and to retain the heat within a furnace or kiln—a highly porous material should be used.

It is not generally known that the porosity of a material appears to have no definite relation to its insulating power; the latter is more closely connected with its permeability. It is a fact that all the best heat-insulating materials are very porous, yet some very porous materials are not good insulators (see also Chapter XIII).

Effect of Porosity on Resistance to Corrosion.—Any article of burned clay or other refractory material having a high porosity is seldom very resistant to corrosion, unless the pores are extremely small. Pores of medium or large size provide cavities which the corrosive materials readily enter and present a large surface to be corroded (see also p. 30). Hence, highly porous materials should not be used where there is much risk of corrosion, either at ordinary or at high temperatures.

In this connection it may be noted that porous bricks and other articles made of fireclay are very liable to have carbon deposited in their pores at high temperatures, as a result of the dissociation of carbon monoxide and hydrocarbon gases which may come in contact with the bricks. The burned fireclay appears to have a catalytic action, the precise nature of which is not understood. The action is largely dependent on the presence of a sufficient surface of unfused fireclay, as dense fireclay bricks with a slightly vitrified surface are only very slightly affected (see also Chapter XI).

Effect of Porosity on Resistance to Abrasion and Erosion.—Highly porous bricks and similar articles usually offer little resistance to abrasion and erosion, because the porous structure exposes a larger surface to the abrasive agent and also reduces the amount of solid matter in a given area or volume of the material.

The effect of porosity on resistance to erosion by wind, rain, etc., appears to be irregular and no definite relation has been found between porosity and weathering. Under ordinary climatic conditions a porous material should be less able to resist the action of the weather than a dense material, but this is not always the case. When the pores in a material are small they absorb moisture which, in cold weather, may freeze and the ice in forming may, by its expansion, partially disintegrate the material. The matter has not been fully investigated, but there is evidence to show that if the pores are sufficiently large, yet not too numerous, no harm will be done. Articles which are only slightly porous do not absorb water readily, so that disintegration does not usually occur, but if a mass of material has a vitrified exterior with one or more cracks or other defects giving access to a porous interior, the damage by frost is likely to be serious. This is specially noticeable with glazed bricks, glazed terra-cotta, etc.

Completely vitrified articles, such as blue bricks, paviours, etc., appear to be quite unaffected by frost. Building bricks are fairly porous, yet, when well made and properly burned, they are very resistant to the weather. Firebricks of all kinds, saggers, retorts, and refractory articles generally, are much less resistant, and should be stored in a warm, dry place, where they will not be exposed to frost.

Bricks and other materials which have been "steamed" during the process of manufacture are not resistant to frost, probably on account of their usually having a porous interior and a dense exterior, the latter having been caused by condensation. Such a structure appears to be very sensitive to frost (see also Chapter IV).

Effect of Porosity on Electrical Conductivity.—Those ceramic materials which have a high porosity usually have a low electrical conductivity. This is probably due to the fact that the decrease in the volume of the solid matter involves an increased resistance to the passage of an electric current, air being a very poor conductor. Many refractory materials are naturally poor conductors, but they are still poorer when they are very porous. On the other hand, some of the best electrical insulators are composed of stoneware or porcelain, which is completely vitrified and devoid of pores. This is largely due to the fact that an electric current will sometimes jump across an air-space or pore when it would not pass through a solid, vitrified mass of clay (see also Chapter XIV).

Effect of Porosity on Dielectric Strength is discussed in Chapter XIV.

Effect of Porosity on Strength.—If a series of pieces of burned ceramic material is made up in such a manner that each member of the series increases progressively in porosity, it will usually be found that the more porous pieces have much less mechanical strength than the denser ones. This must, obviously, be the case, as the greater the porosity the less is the proportion of solid material and the more imperfect the union between the grains comprising the mass (see also p. 31). For most purposes the fired ceramic materials have ample crushing strength and where it is important to do so, almost any desired porosity may be attained. In some cases, however, some of the porosity must be sacrificed in order to obtain sufficient strength.

According to Bleininger,[1] the porosity of clay bricks is inversely proportional to the crushing strength, so that $C=K\frac{1}{P}$, where C is the crushing strength, K is a constant, and P is the porosity. The constant K varies with each particular product, but the formula appears to be applicable when comparing articles made from the same material under the same conditions, but with different porosities (see also Chapter IV).

Effect of Porosity on Refractoriness.—In the strictest use of the term "refractoriness" there is no connection between it and the porosity, but in actual use, porous bricks, saggers, retorts, etc., often appear to be more refractory than those of lower porosity. This is due partly to the fact that their thermal conductivity is lower and, therefore, a longer heating is necessary to produce appreciable signs of fusion, and partly to the fact that porous materials of this nature are often of coarser texture and this further reduces their thermal conductivity. If the heating is sufficiently prolonged, or the test piece is sufficiently small, both porous and dense materials—if of precisely the same composition—are of equal refractoriness (see also Chapter XIII).

Effect of Porosity on Discoloration.—Any porous material is much more liable than a dense one to discoloration, because the former has a greater power of

[1] *Trans. Amer. Cer. Soc.*, **12**, 582 (1910).

absorption. Hence bricks, tiles, and other porous architectural clay wares soon have their surface pores clogged with soot, dust, and other fine particles which discolour the surface and often give it an unpleasant appearance. Close-textured architectural work, such as "terra-cotta," on the other hand, remains clear for a much longer period. Glazed bricks, etc.—which are quite impermeable so long as the glazed surface remains undamaged—are often used in building, as no dust or dirt is absorbed, and that which merely adheres to the surface can readily be removed by washing. If the glazed surface becomes defective (*e.g.* by cracking or crazing), the dirt penetrates the defective portions and cannot easily be removed.

Many roofing tiles are made with a rough and porous surface, so as to make algæ and other vegetable growths adhere more closely and so give them an "ancient" appearance.

Closely allied to discoloration is *efflorescence* or "scum," which is more liable to occur on porous bricks, etc., than on denser ones. Efflorescence is chiefly due to the absorption of salts in the course of manufacture or storage, or from the mortar in which the bricks are laid; the salts are brought to the surface in solution and are left there as a scum when the water which dissolved them has evaporated (see also Chapter III).

Effect of Porosity on the Rate of Drying.—The porosity of moulded articles determines, to a large extent, the speed at which they can be dried. A porous or open body can be dried quickly, because water-vapour can readily escape, whereas a close-textured body does not so easily permit its removal. For this reason it is very desirable that large blocks, etc., should be as porous as possible in the green or unfired state, though this property is often extremely difficult to control. The rate at which fired articles can be dried after they have been wetted also depends on their porosity, though still more on their permeability (p. 89; see also Chapter VII).

Effect of Porosity on Uses.—From the preceding pages it will be seen that porosity is an extremely important factor and one which must be carefully considered if satisfactory articles are to be produced. No very definite rules respecting it can be formulated and in deciding what amount of porosity is required in an article or material for any particular purpose, it is necessary to know fairly fully the conditions to which the articles will be subjected.

The porosity of raw ceramic materials, other than moulding sands and some other refractory materials used in the loose or powdered state, is not usually of great importance, as the positions and relative distances between the particles are changed considerably when they are made into articles. The porosity of raw clays varies greatly according to their nature. Some plastic clays appear to be devoid of porosity, some fireclays have only about 3 per cent. porosity, whilst some sandy loams have a porosity of 25 per cent. or more. Some clays which have a very low porosity in the damp state will absorb a large amount of water in excess of that previously present if they are first dried and then soaked in water. Use is made of this property when it is desired to soak clays in pits prior to converting them into a highly plastic paste of suitable consistency for moulding.

The amount of water absorbed by dry clay is often considerable, in some cases

being as much as 80 per cent. by weight. This absorptive power is due, according to Rohland, to the colloids present in the clay, and is dealt with in Chapter VI. It may also be due to the capillary structure of the clay particles. In any case the total absorptive power of a plastic clay is not strictly proportional to the volume of the pores, as more water appears to be absorbed than is required to fill the pores, and the absorption is also accompanied by a swelling of the material similar to, but far less than, that of glue.

Kerl divides burned clay-wares into two divisions, according to their porosity, as follows :—

1. *Porous ware*, including bricks, tiles, terra-cotta, refractory ware, coarse pottery, earthenware, and pipes.

2. *Impermeable ware*, including stoneware, china ware, and porcelain.

These divisions are only general, however, as some bricks are quite impermeable to water, and some china ware is appreciably porous.

Building bricks should be moderately porous, as otherwise when moisture condenses from the air, the resultant water collects in drops on the inside of the walls, spoiling the wallpaper and giving the impression that the building is damp. If the pores are sufficiently minute, the bricks may be as highly porous as possible. The more porous they are, the better will the walls " breathe." Bricks with large, coarse pores should be avoided, as they admit rain water too easily, but do not always part with it readily, so that walls in which they are used often remain permanently damp. The porosity of ordinary building bricks should not usually exceed 20 per cent. by weight or 50 per cent. by volume. Common red bricks and facing bricks usually have a porosity of 5–10 per cent. by weight or 12–20 per cent. by volume, whilst wire-cut bricks, rubbers, and gault bricks usually have a porosity of 12–20 per cent. by weight or 30–55 per cent. by volume.

In the south of England, the average amount of water absorbed by bricks during complete immersion is about 12 per cent. of the weight of the brick. North of the Trent and in Wales, somewhat denser bricks are usual and the average water absorption is seldom over 8 per cent. of the weight of the brick.

Bricks made by the semi-dry process—that is, by compressing the clay in the form of a damp dust—absorb only about 5 per cent. of water, though they vary greatly in this respect.

For all ordinary purposes, therefore, it is not desirable to designate bricks which absorb less than 15 per cent. of their weight of water on immersion as particularly porous. Good bricks should absorb water slowly and should part with it readily when exposed to a dry atmosphere.

Bricks and other articles which are required to resist chemical action at ordinary or moderately low temperatures, or which must possess great strength, must be denser than ordinary architectural materials. Blue bricks of good quality usually have a porosity of only 0·1–2 per cent. ; it should not generally exceed 3 per cent. by weight. Obsidianite bricks have a porosity of about 0·3 per cent. The American Society for Testing Materials [1] specifies the following porosity for bricks for sewers :—

[1] Vol. **21**, 527–32 (1921).

	Mean Porosity per cent. by Weight.	Maximum Porosity per cent. by Weight.
Class A, vitrified . .	3 or less	. .
Class B, ,, . .	5 or less	6·0
Hard	5–10	12·0
Medium	10–15	17·0

H. Burchartz [1] has suggested a porosity of 5 per cent. by weight, or 10 per cent. by volume, for clinker bricks, and 8 per cent. by weight, or 16 per cent. by volume, for hard-burned sewer bricks.

The large hollow blocks used in fireproof floors, etc., are usually made of a highly porous material. This not only reduces the cost of carriage and the weight of material in the structure, but it facilitates manufacture of blocks accurate in shape and free from twists.

Tiles, *terra-cotta* and other unglazed argillaceous building materials should have a similar porosity to building bricks, but the exposed surface should be non-porous.

According to W. G. Worcester,[2] the best roofing tiles should have a porosity between 3 and 18 per cent., light red tiles having a porosity of 10–18 per cent., and the darkest and densest red tiles a porosity of 3–4·5 per cent.

Other *unglazed wares* should have a porosity corresponding to the purpose for which they are to be used. Such articles as flower-pots, filters, etc., must be very porous.

Refractory Articles.—The porosity of *fireclay bricks* is often much more important than in bricks which are not heated to a high temperature. It varies very considerably according to the purposes for which the bricks are to be used, but is generally between 8 and 24 per cent. by volume or 3–9 per cent. by weight. Where there is little corrosion or abrasion, a highly porous brick may be quite satisfactory and, even where these actions do occur, a porous brick may be necessary in order to give the requisite resistance to sudden changes in temperature. In the checker-work of regenerators, the conditions required demand two opposite qualities ; great resistance to sudden changes of temperature, consequent upon passing cold air amongst the hot bricks, which necessitates the use of porous bricks, whilst the high thermal conductivity necessary to obtain a maximum heat capacity is obtained only by using close-textured bricks. In practice, a compromise is effected by using bricks of moderate porosity.

In some other cases, the difficulty may be overcome by the use of bricks having a porous interior to resist temperature changes and a dense surface to resist corrosion and abrasion (see also p. 61). Bricks of this type are largely used in blast-furnaces,

[1] *Mitt. Königl. Materialprüfungsamt*, **34**, 79 (1916).
[2] *Geol. Survey of Ohio, Bull.*, **11**, 121.

recuperators, calcining furnaces, coke ovens, crucible furnaces, chemical furnaces, retort settings, reverberatory furnaces, frit kilns, etc. Highly porous bricks are required in the roofs of coke ovens on account of the great changes in temperature to which they are subjected. The walls must be denser so as to be sufficiently resistant to corrosion and abrasion. One well-known firm of coke-oven builders specifies that firebricks for this purpose should have a porosity of not less than 12 per cent. by volume or 6 per cent. by weight.

According to a Provisional Specification, published by the Society of Glass Technology, the porosities of *glass-tank blocks* made of fireclay should be as follows :—

Flux-line blocks . . .	Porosity	not	more	than	18 per cent.
Replacement flux-line blocks .	,,	,,		23	,,
Bottom side blocks . .	,,	,,		25	,,
Tank bottom blocks . .	,,	,,		30	,,

Porous fireclay bricks, when heated to redness, decompose carbon monoxide, liberating free carbon. This is undesirable, especially in gas producers, etc., used in the production and utilization of carbon monoxide gas.

In general, when the articles are to be heated to a high temperature, they should be as porous as is consistent with the other properties required.

Saggers should generally have a porosity of 10–40 per cent. by volume or even greater, provided the pores are very small and do not allow the fire-gases to enter into the interior of the sagger and so discolour the goods, and that the saggers possess sufficient strength.

Muffles should have as porous a structure as possible, so that they will permit sudden heating or cooling. Muffles which are too dense are not economical in fuel, as they require a much longer time to heat, as well as to fire the goods.

Glass-house pots should have a porous coarse texture, but both the inner and outer surfaces should be dense so as to resist the corrosive action of the molten glass and the flames.

Retorts should have as high a porosity as is consistent with the other requirements, so that they may be resistant to changes in temperature. Too great a porosity must be avoided, however, where resistance is required to fluxes, ash, etc. The Institute of Gas Engineers specifies that the porosity should not be less than 18 per cent. by volume ; in Germany many retorts have a porosity of 25 per cent. The porosity of gas retorts which have been in use some time is reduced by the deposition of carbon in the pores of the material. The porosity of zinc retorts may be as high as 26 per cent. by volume when first used, but after a few days the porosity is rapidly diminished and may be as low as 1·5 per cent. on the seventh day.

According to Babcock,[1] the bond clays for zinc retorts should have a porosity of 10 per cent. by weight after being fired at 1150° C., and 5 per cent. after being fired at 1250° C.–1400° C.

The porosity of *silica bricks* may vary very considerably, though the usual limits are 15–32 per cent. by volume. It has been found by the author that bricks with a

[1] *J. Amer. Cer. Soc.*, **2**, 83 (1919).

porosity of about 18 per cent. usually give the most satisfactory results. One well-known firm of coke-oven builders specifies a porosity of not less than 12 per cent. by volume and 6 per cent. by weight for silica bricks to be used in coke ovens.

Silica cements used for firebricks, according to R. J. Montgomery,[1] vary in porosity from 30–35 per cent. at Seger cone 1a (1100° C.) to 15–30 per cent. at Seger cone 20 (1530° C.).

Kieselguhr is highly porous and can absorb as much as $2\frac{1}{2}$ times its weight of water without appearing to be wet. When mixed with fireclay, the resultant articles are so porous that they are very easily corroded and abraded, so that they should be carefully protected from these actions. On account of their porosity and permeability they are very valuable as heat insulators.

In *moulding sands*, porosity is very important, as when molten metal is poured into the mould the gases produced must be capable of escaping readily, or they may cause blowholes and other troublesome defects in the metal itself. On the other hand, excessive porosity is undesirable, as it causes the castings to have an irregular surface and much of the sand to adhere to the metal when cooled.[2]

Sand for lining open-hearth furnaces should have as dense a texture as possible so as to prevent the excessive absorption of slag [2] (see p. 42).

Magnesia bricks should have a low porosity or a dense structure; when struck they should give a clear, ringing note. This low porosity is necessary because such bricks are largely used under conditions where there is a considerable risk of corrosion by basic slags. Where they are not subject to corrosion, bricks with a porosity up to 40 per cent. by volume may be employed. According to M'Dowell and Howe,[3] ordinary magnesia bricks should have a porosity of 24–30 per cent. by volume, though many Austrian and German magnesite bricks have a porosity of only 18–21 per cent. After prolonged use at a high temperature, the porosity may be reduced to as low as 10 per cent.

Zirconia articles with a lime or kaolin bond usually have, according to A. Bigot,[4] a porosity of 4–7 per cent.

According to O. Ruff and G. Lauschke, zirconia crucibles become less porous the higher the burning temperature, though in apparent opposition to this statement these investigators found that the most porous crucibles were produced from zirconia which had been calcined at 1500°–2200° C. Beryllium oxide, magnesia, alumina, thoria, and yttria reduce the porosity of zirconia crucibles. The first three oxides are volatilised above 2000° C., but thoria and yttria reduce the porosity at still higher temperatures.

Asbestos bricks are highly porous and, therefore, withstand sudden changes of temperature, but they are not resistant to the action of fire-gases, slags, and other corrosive agencies.

[1] *Amer. Soc. for Testing Mtls.*, 1918.

[2] For further information see the author's *Sands and Crushed Rocks : Their Nature, Preparation, and Uses* (Frowde, Hodder & Stoughton).

[3] *J. Amer. Cer. Soc.*, **3**, 185–246 (1920).

[4] *Céramique*, **37**, 191–3 (1919).

Stoneware should be devoid of porosity, but this is seldom attained, and the commercial articles absorb 0·5–2 per cent. of their weight of water. They should not exceed the latter amount.

Porous bisque, or *Biscuit ware*, is an intermediate product in the manufacture of glazed ware. It is fired prior to glazing to give it greater strength in the dipping and decorating processes and to enable the glaze to adhere well to the surface. A suitable porosity is 10–15 per cent. by weight. Excessive porosity is undesirable, as too much of the glaze is then absorbed by the ware ; this not only wastes glaze, but tends to cause warping and produces a dull surface.

China ware and porcelain of the best quality should, when glazed, have a porosity not exceeding 2 per cent. when broken pieces are tested. Some of the best vitrified porcelains have a porosity of only 0·05 per cent.

Semi-porcelain may have a porosity of 13–23 per cent. according to its nature.

A good test for the porosity of vitrified ware, and for the white engobes used on sanitary ware, is to immerse the article in a 0·5 per cent. solution of eosin or ordinary red ink for 18 hours, and then rinse, dry, and examine with a lens. There should be no staining.

Table XVII, due to Harvard, shows the average porosity by volume of various types of clay and ceramic materials :—

TABLE XVII.—*Porosity by Volume of Ceramic Materials*

	Burning Temperature, ° C.	Porosity per cent. by Volume.
Fireclay bricks	1050	30·8
,, ,,	1300	24·1
Checker bricks	..	27·8
Bauxite bricks	1300	38·4
Silica bricks.	1050	42·58
,, ,,	1300	42·9
Magnesia bricks	1300	41·0
,, ,,	1050	35·1
Carborundum bricks	1050	35·2
,, ,,	1300	30·6
Chromite (unburned)	..	21·3
Chromite bricks with clay bond	1300	26·4
Kieselguhr	..	38·0
Graphite bricks	..	26·0
Building bricks	1050	25·7
Light clay	..	45·7

Determination of the Porosity and Absorption.—As explained on p. 61 there is a distinction between the true and apparent porosity, but in most cases the term " porosity " is applied to the apparent porosity as estimated from the amount of water and other suitable fluid absorbed by a given weight or volume of the sample. Hence, the *absorption* or *apparent porosity* is a measure of the unsealed pores. It is usually determined by weighing a whole brick, or a conveniently sized sample, and immersing it in water for several hours, after which it is removed, the surface moisture wiped off with a cloth, and the test piece re-weighed. The gain in weight is the water absorbed ; if this is multiplied by 100 and divided by the weight of the dry sample, the result will be the percentage porosity *by weight*. The percentage of apparent porosity by volume may be found by the following formula :—

$$p = \frac{100\ \mathrm{P}s}{100 - \mathrm{P}s},$$

where p=percentage of porosity by volume, P the percentage of porosity by weight, and s the apparent specific gravity of the solid material.

The apparent porosity by volume may also be found by the following method : (*a*) weighing the sample ; (*b*) suspending the sample in water from one end of the arm of the balance by a fine thread and weighing it whilst thus suspended and immersed ; (*c*) wiping off the surplus water and weighing the sample whilst saturated with water. Then

$$\mathrm{P} = \frac{100(\mathrm{W} - w)}{\mathrm{W} - i},$$

where P is the percentage of apparent porosity by volume, W the weight of the sample when saturated with water, w the weight of the dry sample, and i the weight of the sample when immersed in water.

When determining the apparent porosity, the sample should not be completely immersed at first or air may remain trapped in the pores and, not being able to escape, will give a low result for the porosity. It is much better to arrange that the sample is only partly immersed at first, so as to give the air an opportunity of escaping. Later, it may be completely covered and then left in this condition for several hours, so as to ensure the complete filling of the open pores with water.

Where a more accurate result is required, the sample may be boiled in water for about an hour, instead of merely immersing it in cold water. This will give sufficiently accurate results for most purposes, but where the most accurate results which can be obtained are required the sample may be first boiled, then subjected to a vacuum of 29 inches of mercury for 3 hours and afterwards immersed in water at normal temperature for 96 hours. Table XVIII, due to R. C. Purdy and J. K. Moore,[1] shows the effect of using a vacuum.

The increase is specially noticeable with dense materials. Purdy and Moore suggest that 15 minutes of vacuum treatment is usually sufficient after a 48-hour saturation.

[1] *Trans. Amer. Cer. Soc.*, **9**, 211 (1907).

TABLE XVIII.—*Effect of Vacuum in Porosity Determination*

Sample.	Porosity after 48 hours' Saturation without Vacuum.	Percentage Gain in Porosity after Vacuum Treatment for—			
		5 min.	10 min.	15 min.	20 min.
S 2	3·22	48·10	51·80	57·90	65·00
G II	3·30	38·70	42·10	48·40	50·60
K 46	3·93	27·30	..	35·60	37·50
K 15*d*	4·22	13·48	14·48	18·70	20·80
K 13*c*	4·27	44·60	46·60	46·60	46·60
K 15*c*	4·51	33·40	36·50	36·80	38·20
R 4	5·12	58·20	59·40	61·70	63·70
H II	5·29	31·20	35·40	37·60	38·90
R 2	6·10	27·50	32·20	35·60	36·00
K 6*d*	6·46	29·90	31·60	35·30	39·30
K 2	6·55	18·60	20·10	21·60	24·30
R 1	6·70	10·20	11·00	11·00	11·00
B II	6·91	28·00	30·40	31·40	32·00
J II	7·53	11·80	13·70	15·70	16·00
I II	8·64	11·80	12·80	14·10	14·80
K 8*d*	9·06	22·00	23·50	24·00	24·90
B I	9·39	13·11	20·30	23·40	..
K 15*b*	19·80	6·05	6·22	6·84	7·34

H. D. Foster [1] found that the vacuum treatment has an efficiency of 97 per cent. as compared with 92 per cent. when the sample is soaked for 72 hours in cold water.

In many cases, it is important that a whole brick or article should be used when making porosity tests, because the surface is usually rather more dense than the interior and, if a portion of an article is employed, a higher result will be obtained. For this reason, when a broken article or only a portion of an article is used for the test, this fact should be specified.

The American Society for Testing Materials specifies the following porosity test: "At least five half bricks shall be first thoroughly dried to constant weight at a temperature of from 200° to 250° F., weighed and then placed on their faces in water to a depth of 1 inch in a covered container. The bricks shall be weighed at the following intervals: ½ hour, 6 hours, and 48 hours. Superfluous moisture shall be removed before each weighing. The absorption shall be expressed in terms of the dry weight and the balance used must be accurate to 5 grams."

[1] *J. Amer. Cer. Soc.*, **5**, 788 (1922).

If, on the other hand, the test is made to ascertain whether the interior of an article is uniform in character or has been properly fired, it is usually necessary to measure the porosity on a portion of the article and not on the whole. In testing pipes, portions of the sample are invariably employed. The following method is adopted by various American Associations :—

" The specimens shall be each approximately 2 inches square and shall extend the full thickness of the pipe wall, with the outer skins unbroken. Five individual tests shall constitute a standard test, the average of the five and the result for each specimen being given in the report of the test. Each specimen shall be dried in an oven, or by other application of artificial heat, until they cease to lose further appreciable amounts of moisture when repeatedly weighed. All surfaces of the specimens shall be brushed with a stiff brush before weighing the first time. The specimens shall be weighed immediately before immersion on a balance or scales capable of accurately indicating the weight within one-tenth of 1 per cent. The specimens shall be completely immersed in water for a period of twenty-four hours. Immediately upon being removed from the water the specimens shall be dried by pressing against them a soft cloth or a piece of blotting-paper. There shall be no rubbing or brushing of the specimen. The re-weighing shall be done with a balance or scales capable of accurately indicating the weight within one-tenth of 1 per cent. The result of each absorption test shall be calculated by taking the difference between the initial dry weight and the final weight and dividing the remainder by the initial dry weight."

Mellor [1] suggests that porosity should be determined on samples roughly cubical in shape and having sides about 2 inches long, whilst Wologdine and Queneau use samples weighing only 10 grams. The figures obtained from small samples are not comparable with those obtained with whole articles.

The *true porosity* cannot be determined directly, as it not only includes the pores which can be filled by immersing the mass in water (*i.e.* apparent porosity), but also any sealed pores to which no fluid can gain access without destroying the mass by grinding it to powder. The volume of the sealed pores is very difficult to determine, and can only be arrived at indirectly from measurements of the specific gravity, weight, and total volume of the material as proposed by Heath and Mellor. The true porosity may then be estimated from the formula

$$P=100\left(1-\frac{W}{SV}\right),$$

where P is the true porosity in terms of per cent. by volume, W the weight of the dry sample, S the specific gravity of the material when in the form of a fine dry powder, and V the volume of the sample, including the pores. According to R. C. Purdy,[2] the volume of sealed pores is equal to $\left(\frac{T-A}{T}\right)100$, where T is the true specific gravity and A is the apparent specific gravity.

[1] *Trans. Eng. Cer. Soc.*, **17**, 314 (1917–18).

[2] *Trans. Amer. Cer. Soc.*, **11**, 60 (1909).

It has been suggested that the porosity is equal to the product of the percentage absorption and the specific gravity, but this has been shown by Purdy and Moore to be incorrect.

Rough tests for comparing the absorption or apparent porosity of various materials are :—

(*a*) If on holding the sample to the tongue a distinct suction is felt, the sample may be described as " very porous." If there is no distinct suction, but the moisture is absorbed rapidly, it may be described as " moderately porous," whilst if the moisture is very slowly absorbed, it is only " slightly porous."

(*b*) A rough test of the speed with which water is absorbed consists in immersing the sample to half its depth in water and noting the rapidity with which the water rises into the other half. This is a rough indication of its capillarity rather than its porosity, but the two are often closely related. It is desirable to make several tests on different articles or samples of the same nature, as many clay products and ceramic materials are not always uniform and the average of several tests is more likely to be representative than the result of any one test. This is especially necessary where only a small sample is used, as different parts of the same article may vary considerably in porosity.

When the porosity by volume of an irregularly shaped sample is required, it is most convenient to use a volumeter. The two types generally employed are Ludwig's and Seger's respectively. Ludwig's volumeter (fig. 8) consists of a flanged cylinder with a tap near the bottom, covered with a flanged conical cap, the apex of which is widened out to form a short funnel. The flanges should fit perfectly so as to give a water-tight joint, and the cover is held in place by means of a heavy metal ring placed over the flange. The cylinder is filled with water to a mark on the stem of the funnel, part of the water is then drawn off the tap into a tared vessel. The cover is removed and the sample carefully placed in the cylinder without spilling any water. The cover is replaced and sufficient water poured from the tared vessel back into the volumeter, so that the water is again at the mark on the stem of the funnel. The water remaining in the tared vessel is then weighed; its weight in grams is equal to the volume of the sample in c.c.

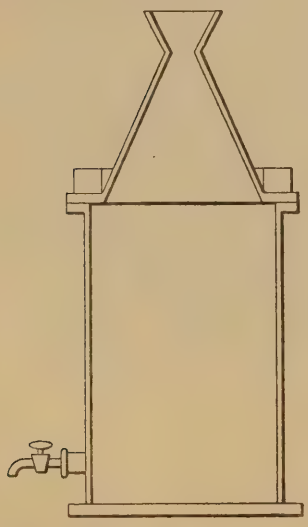


Fig. 8—Ludwig's Volumeter.

Seger's volumeter (fig. 9) is more delicate, but is easier to use, as the water is drawn by suction into a burette and is measured instead of weighed. Otherwise, the two instruments are used in a similar manner.

In determining porosity by means of a volumeter the weight of the sample when dry and also when saturated is found, and then, whilst the sample is still saturated, its volume is determined in the volumeter. The porosity by volume is—

$$Pv = \frac{(W_1 - W_2)100}{V},$$

where Pv is the percentage of porosity by volume, W_1 the weight in grams of the sample when saturated with water, W_2 the weight in grams of the sample when dry, and V the volume of the saturated sample in c.c. as measured by the volumeter.

A rather more accurate result may be obtained, as suggested by Heath and Mellor, by withdrawing nearly all the water from the container into the burette or into a bulb above it, the jar being tilted if necessary. After closing the stop-cock of the burette the weighed sample is placed in the container, the stopper is replaced, and a suction pump connected to the tube in the stopper so as to exhaust all the air in the container. The action of the pump is continued for fifteen minutes so as to remove the air from the sample, after which the stop-cock of the burette is opened and the water run into the jar until the sample is covered, after which the pump is disconnected and the water run in until it reaches the mark on the tube in the stopper. The difference between the readings of the burette when the jar is filled with water and when the sample is present is the volume of the solid matter plus that of any sealed pores. This figure may be designated A. The water is again drawn back into the burette, the soaked sample is replaced, the water is returned until it reaches the mark in the stopper and the burette is re-read. The difference between this reading and the one when no sample is present gives the total volume of the material and pores. If this is designated B the percentage of apparent porosity by volume is $100\,\frac{(B-A)}{B}$.

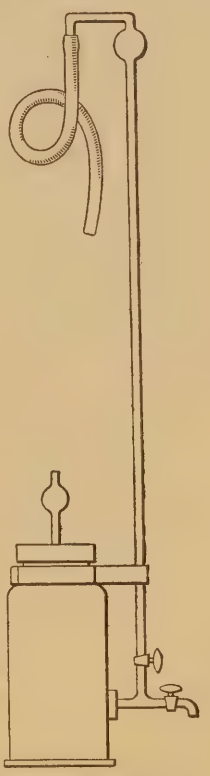


FIG. 9. — SEGER'S VOLUMETER.

The liquid generally used in volumeters is water, but in determining the volume or porosity of substances affected by water, paraffin or other inert liquid may be used. According to Washburn and Bunting,[1] vaseline is preferable to paraffin, kerosene, etc., because of its greater penetrating power and the fact that it can be heated without risk.

All these media have the disadvantage that the sample must be soaked before its volume can be measured, on account of the penetration of the liquid into the pores. Where it is not desired to soak the sample it may be thinly coated with melted paraffin wax, which, when solidified, will prevent any liquid penetrating into the pores. For fine-grained materials mercury may be used instead of water, as it will not penetrate into the article and does not wet it like water and similar liquids.

The use of liquids for porosity and absorption tests is not entirely accurate on

[1] *J. Amer. Cer. Soc.*, **4**, 983 (1921).

account of the slowness with which they are absorbed. Washburn and E. N. Bunting [1] have devised a method of using gas as the pore-filling medium, and have thereby obtained results which are, in some cases, considerably higher than when a liquid is used. The gases they employed include dry air, hydrogen, and helium ; the results obtained with each gas were the same in each case.

The porosity of powders and other loose materials may be determined by placing a definite volume (say 600 c.c.) of the material into a graduated glass cylinder holding 1000 c.c. The mixture should be just shaken down, but not compressed at all. A definite volume of water is then poured in and the cylinder is allowed to stand a little while until the water has filled the pores in the material, after which the resultant volume is measured. The volume of the voids in the loose mixture may be found by subtracting the final volume of the mixture and water from the sum of the volumes of sample and water separately and from these figures the percentage by volume can readily be calculated. Thus, if S is the volume of the sample, W that of the added water, and M that of the mixture, the percentage porosity by volume P will be—

$$P = \frac{(S+W-M)100}{S+W}.$$

The apparent porosity of a loose material will be low if the sample is not perfectly dry, as the moisture present occupies some space which would otherwise be occupied by air. If the particles of a loose material contain no sealed pores, the apparent and true porosity will be identical and can be found from the following formula :—

$$\text{Porosity per cent. by volume} = \frac{100(S-A)}{S},$$

where S is the true specific gravity and A is the apparent density. Thus, if the mixture has a true specific gravity of 2·6 and an apparent density of 1·7, the theoretical porosity will be 34·6 per cent. by volume. Unless the particles are extremely small or devoid of sealed pores, the porosity so calculated is rather higher than that determined directly from the absorption of water or other liquid. The difference is due to sealed pores and to fissures in the grains which are too small for the liquid to penetrate.

Penetrability is a term which is not commonly used ; it is defined by E. W. Washburn as the ease with which a liquid is drawn into the pores of a body by capillary action without attendant chemical action between the body and the liquid. It is measured in a similar manner to the apparent porosity, which it closely resembles.

Permeability

Permeability may be defined as the readiness with which a substance permits a fluid to flow through it and is measured by the rate at which a standard fluid, such as water, air, or other gas, flows through a mass of unit area and unit thickness. As pressure is necessary to cause the flow, it is necessary to specify the pressure or

[1] *J. Amer. Cer. Soc.*, **5**, 112 (1922).

head of the fluid. Water is usually employed, but air or other gas, being much more mobile, gives more accurate results.

The velocity of flow of water through a capillary tube is expressed by the formula $V=\frac{r^2P}{8ul}$, where V is the velocity in cm. per sec., r is the radius of the tube in cm., P is the difference in pressure at the ends of the tube in cm., u is the viscosity of the liquid, and l is the length of the tube in cm. The force which causes the water to flow is equal to $2\pi r\mathrm{T}\cos a$, where T is the surface tension and a the angle of contact between the water and the walls of the pore. When the water is rising the force which is against it is πr^2hpg, where h is the height to which the water has risen at a particular moment and g is the force due to gravity, so that the resultant force will be $2\pi\mathrm{T}\cos a-\pi r^2hpg$.

The velocity is approximately proportionate to the cube of the radii of the pores and inversely to the height to which it ascends. Hence, a coarse-grained brick is more permeable to water than a fine-grained one.

To be wholly impermeable, a material must be very compact and close in texture, at any rate on its exposed surface, and for this reason such surfaces are often covered with a glaze. Where a large article has to be repeatedly heated and cooled, a wholly dense material is undesirable on account of the low resistance to temperature changes of most ceramic materials of this nature. Under such conditions the "body" of the article is usually made of a porous, coarse-grained material, the required impermeability being obtained by glazing, either the interior or exterior surface. Instead of deliberately applying the glaze, it may be formed "automatically" during the course of manufacture as a result of the action of fluxes, etc., on the materials of which the articles are made or of the reactions which occur between the articles and their contents. Thus, in coke-ovens, a glaze is often formed by the action of salts in the coal on the firebrick linings and an even thicker glaze is produced in zinc retorts which eventually renders them quite vitreous.

In paving bricks and tiles, porcelain and some forms of stoneware, the requisite impermeability is produced by the interaction of fluxes and the material of which the goods are made, with the result that the greater part of the pores present in the early stages of firing are later filled with a glassy mass of fused silicates which renders the article impermeable. The production of impermeable articles is costly and in many cases both unnecessary and undesirable, but in others it is essential.

The permeability of a mass of clay depends on its plasticity and moistness. If a clay is quite dry its plasticity is dormant and it will be readily permeable to water, yet the same clay when wetted and its plasticity made "active" will be impermeable to water.

The permeability of an article depends on (*a*) its thickness; (*b*) the kind, number, distribution, and sizes of the pores; (*c*) the presence or absence of cracks, fissures, and holes; (*d*) the presence or absence of a superficial glaze or slag; (*e*) the difference in pressure on opposite sides; (*f*) the nature of the penetrating fluid; and (*g*) the difference in the temperature of opposite sides of the article.

In several of these respects permeability differs greatly from porosity (p. 61),

for whereas the latter is a measure of the total volume of the pores, the permeability depends on the extent to which they penetrate through the mass. A glazed brick may have a high porosity, but it should, when in use, be impermeable so long as the glaze is undamaged. In other words, permeability depends chiefly upon the number of channels or connected pores which enable the permeating liquid to pass through from one side of the article or test-piece to the other. Pores which are closed at one end, or do not penetrate far into the mass, take no part in producing a permeable mass; a single small crack penetrating right through the mass may increase the permeability more than a thousand short or disconnected pores. In short, whilst highly porous articles are often highly permeable, there is no definite relation between the porosity and permeability of a material and a tile may have a true porosity of 25 per cent. and yet be impermeable even to gases.

The absence of any relation between porosity and permeability is well shown in Table XIX, containing figures obtained by A. L. Queneau.

TABLE XIX.—*Porosity and Permeability*

	Porosity, per cent. by Vol.	Permeability in litres per hour per sq. m.
Glass pot . . .	30·00	0·30
Glass pot . . .	30·40	1·02
Firebrick . .	29·44	37·84
Firebrick . . .	30·85	14·72
Firebrick . . .	30·20	106·20
Silica brick . .	42·58	3·32
Silica brick . .	42·90	192·90

The permeability of an article, especially to gases, sometimes varies in different directions, especially if the material is laminated. This subject has not received the attention it deserves.

The maximum permeability in one direction is possessed by a structure composed of a large number of minute (capillary) tubes, arranged parallel to each other. Apart from the resistance caused by the surface tension of the walls of the tubes such a "honeycomb structure" would be completely permeable. In the ceramic industries, no materials are known which possess this structure, so that the permeability is usually due either to fissures or cracks in the materials or to numerous pores being connected and so forming irregular channels.

Effect of Heat on Permeability.—When ceramic materials are heated, allotropic and other changes which occur—especially in fireclay, silica, and magnesia—may cause large changes in the permeability and density without greatly affecting the other properties of the mass. Thus, A. L. Queneau [1] has shown that a silica brick

[1] *Electrochem. and Metal. Ind.*, **7**, 385 (1909).

burned at 1050° C. had a permeability of 3·3 litres per hour, whilst that of a brick made of the same material, but burned at 1300° C., was 193 litres, and the permeability of a brick burned at 1400° C. was 241 litres per hour. Fireclay and bauxite bricks also increase in permeability rapidly in this way. At temperatures of 1100° C. and above, articles made of " fused silica " or quartz glass are permeable to hydrogen, oxygen, and nitrogen. This is sometimes serious, as in the case of pyrometer tubes, in which the platinum wires are slowly affected by the gases which permeate the walls of the tubes. At temperatures below 1100° C. this difficulty does not occur, as the " fused silica " is then quite impermeable.

Effect of Permeability on Thermal Conductivity.—As the thermal conductivity depends on the mobility of the air in the pores, it usually increases with the permeability as explained more fully in Chapter XIII, but chromite, magnesia, carborundum, and graphite behave irregularly in this respect. The heat-insulating power at temperatures below 1200° C. is roughly proportional to the permeability.

Effect of Permeability on Drying.—The rate at which a mass or article of clay or other ceramic material can be dried with safety depends largely on its permeability, because the water-vapour escapes more easily and quickly from a permeable material as the pores in it are directly connected with the atmosphere.

Effect of Permeability on Uses.—The purpose for which an article is to be employed is often influenced by its permeability. Thus, in building *reservoirs* and *embankments*, etc., a mass of clay paste or " puddle " is used to prevent the passage of water, as clay paste is almost impermeable. In this respect, it differs from dry clay, which is readily permeable to water. For this reason, when it is desired to prepare a clay paste it is desirable to dry the clay prior to soaking it in water, as the water will then penetrate it much more readily and will be more uniformly distributed through the mass. Unfortunately, the cost of drying is often so great that it is omitted.

Ordinary building bricks should be permeable to air, so that they may " breathe," *i.e.* allow air to pass through them, but they should not be permeable to water, or rain will enter and make the wall " damp." If a house is built with solid walls of impermeable bricks it will appear to be " damp," because the impervious walls cannot absorb the moisture condensed on them during cold weather. Other argillaceous building materials, such as terra-cotta, etc., should usually have similar properties. *Paving bricks* should be quite impermeable.

Roofing tiles should be permeable to air, but not to water, or they will allow rain to pass through them and accumulate on or even drop from the underside of the tiles, thereby causing damage.

Filters should be very permeable, so that they allow water or other liquids to pass through them at a suitably rapid rate. The pores must, however, be sufficiently small to prevent any " dirt " or other undesirable solid matter passing through them. A filter may be tested for permeability by noting the amount of water passed through it in a given time (say twenty-four hours).

Saggers and *muffles* should be porous but not very permeable, or they will not protect the goods from flame, smoke, etc., produced by the fire-gases. This object

is attained by having the pores as small as possible consistent with the articles being resistant to sudden changes of temperature.

Retorts should be porous, but not permeable, or much of the vapour or gas produced in them may be lost. This loss may be reduced by regulating the withdrawal of the vapour or gas, so as to avoid the creation of an appreciable pressure in the interior of the retort. In new gas-retorts, permeability is seldom serious, as the formation of a deposit of carbon on the interior soon prevents any loss of gas by permeation.

In *blast-furnaces* the bricks and blocks used for the lining should not be highly permeable, or, as B. Osann[1] has shown, they will permit carbon monoxide in the gases to reduce the iron oxide in the bricks and cause them to fuse more rapidly than would otherwise be the case.

Graphite crucibles are commonly supposed to be quite impermeable, but this is not the case, as at temperatures above 1200° C. they are permeable to furnace gases.

Glazed ware, *stoneware*, and much *chemical ware* should be quite impermeable (see p. 87).

Table XX, due to A. L. Queneau, shows the permeability of various ceramic materials :—

TABLE XX.—*Permeability of Ceramic Materials*

	Burning Temperature, ° C.	Permeability, c.c. per sec. per sq. cm. through slab 1 cm. thick.	Litres per hour per sq. m. through slab 1 m. thick.
Fireclay brick . .	1050	0·0409	14·72
,, ,, . .	1300	0·0690	24·84
Checker brick. . .	..	0·0465	16·74
Bauxite brick. . .	1300	0·2120	76·39
Silica brick . . .	1050	0·0092	3·32
,, ,, . . .	1300	0·0536	192·90
Magnesia brick . .	1300	0·0097	3·49
,, ,, . .	1050	0·5170	186·10
Carborundum brick. .	1050	0·0053	1·90
,, ,, . .	1300	0·0043	1·55
Chromite (unburned) .	..	0·0568	20·45
Chromite bricks with clay bond	1300	0·0075	1·70
Kieselguhr . . .	..	0·0957	34·45
Graphite bricks . .	..	..	..
Building bricks . .	1050	0·0015	0·53
Light clay . . .	..	0·0164	5·90

[1] *Stahl und Eisen*, 1907, p. 1627.

Determining Permeability.—The permeability of slabs, tiles, and other articles may be determined by fastening a glass cylinder of convenient size to one surface of the article, using a rubber washer or other device to prevent any leakage between the glass and the article, filling the cylinder with water and supporting the article on thin rods, or preferably on knife-edges, over a glass vessel. After twenty-four hours, or a longer period if preferred, the volume of the water which escapes from the cylinder into the vessel below is measured. The area of the part of the article exposed to the water and the pressure or height of the water in the cylinder, should also be recorded. The result gives a relative value for the permeability. Bottles

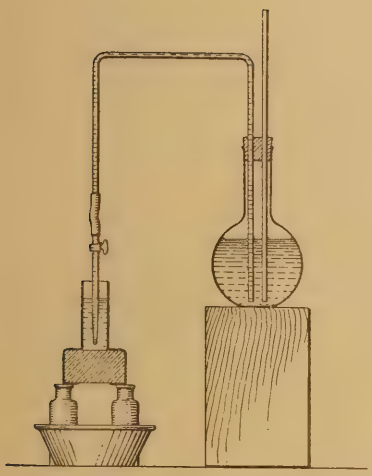


Fig. 10.—Permeability Test.

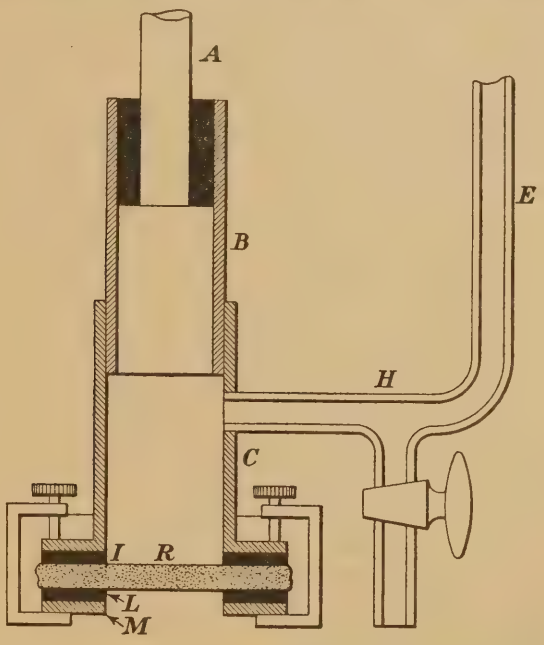


Fig. 11.—Sokoloff's Permeability Apparatus.

are sometimes used instead of cylinders open at both ends, but the results are less satisfactory, as the water tends to be held in the bottle by the pressure of the atmosphere. When testing articles of considerable thickness, such as bricks, it is desirable to paint all the surface, except the parts to which the cylinder is applied and an equal area opposite to it, with a waterproof shellac or varnish. If the article is very permeable it may be kept supplied with water at a constant level by the arrangement shown in fig. 10, the water absorbed being automatically replaced by a fresh supply from the flask.

In this way the time taken for the under-surface of the test-piece to become moist, dew-covered, and to liberate drops of water, can be readily observed, the time taken to pass a prearranged quantity of water through the article can be measured and valuable information as to the relative waterproofness of different tiles, etc., obtained.

A more elaborate apparatus used by Sokoloff (fig. 11) consists of a short cylinder,

C, with a flange at its lower end and a short tube, B, fitted with a rubber cork in its upper end, the joint between the two being made water-tight. Through the rubber cork a long graduated glass, A, sealed at the top with a cotton-wool plug, is inserted. A T-piece tube of metal, H, is fitted into a hole through the side of the flanged cylinder, a little way above the flange, one free end being connected by a pipe, E, to a water supply, placed well above the apparatus and provided with a tap or a pinch-cock, whilst the other end is closed with a second tap or pinch-cock. The sample R should be of the same diameter as the flange and is usually 5 cm. thick, but if water escapes through the edges of the test-piece, a thinner sample must be used. The sample is boiled until saturated with water and is then clamped on to the metal flange with a rubber washer, I, between them, and a rubber, L, and a metal, M, washer below. The upper washer should preferably have an opening about 1 inch in diameter, which should always be kept constant or the results will vary on account of the differences in the area through which the water may permeate. Water is run through the tube E into the tube A, until it reaches a height of exactly 40 inches. The tap is then turned off and the water is allowed to permeate through the sample. The test is continued until 4 inches of water have passed through, the time taken being a measure of the permeability. If desired, pressure may be applied to the liquid in A by means of a pump, but in that case the pressure should be recorded. To ensure accurate results, the temperature of the apparatus and water should be carefully brought to and maintained at 15° C. or 60° F. The taps on the apparatus must fit accurately, and soft, filtered water or distilled water should be used, so as not to choke any of the pores in the sample and so reduce its permeability. The permeability of a material to air or other gases is determined by Wologdine and Queneau [1] on a cylinder of the material, 40 mm. in diameter and about 60 mm. long, coated with paraffin wax and cemented into one end of a glass tube. The other end is closed by means of a rubber stopper fitted with a tube connected to a gas-holder and manometer so as to maintain a constant pressure. Air or gas is applied under a prearranged pressure for a definite period of time and the amount of air passed through the test-piece is measured and reported as the relative permeability of the sample. The two alternative standards suggested by Wologdine and Queneau are (*a*) the amount of air in c.c. under a head of 1 cm. of water which passes in 1 second through a cylinder 1 square cm. cross-section and 1 cm. in height, and (*b*) the number of litres passing in 1 hour through a surface of 1 square cm. 1 metre thick. The latter is calculated from the following formula :—

$$V = \frac{gl}{16{\cdot}667tPS},$$

where V is the permeability in litres passing in 1 hour through a cylinder of 1 square cm. area and 1 metre thick, g the quantity of air, in litres, passing in t minutes under the pressure P (*i.e.* the height of water in cm. in the manometer in excess of that corresponding to atmospheric pressure) through the cylinder of cross-sectional area S and length l. As the permeability very often varies in different parts of the same article on account of holes, minute cracks, etc., it is difficult to obtain a representative figure.

[1] *Electrochem. and Metal. Ind.*, Oct. 1909.

The permeability of a loose powder may be determined by means of the following apparatus used by the author :

A circular metallic box, 3 inches diameter and $1\frac{1}{4}$ inches deep, with a flanged rim at the top, has the bottom cut out and replaced by a piece of wire gauze of any suitable mesh. On this gauze is laid a sheet of thin blotting-paper and the case is filled with the material to be tested to the height of exactly 1 inch. If the material is to be compressed in use, the state of compression should be the same in the test sample. The sample is covered with a second sheet of blotting-paper and a flanged pipe about 4 feet in length is secured to the box and filled with water to a height of 40 inches or 1 metre. The apparatus is suspended over a glass vessel to collect the liquid passing through the sample. The time taken for 100 c.c. of water to pass through the sample is regarded as a measure of the permeability.

CHAPTER III

COLOUR, HARDNESS, AND MINOR PHYSICAL PROPERTIES

SEVERAL of the properties of clay and other ceramic materials described in this chapter are, in many cases, of minor importance, but in some instances they are of major importance. Thus, whilst the colour of raw clays usually matters little, a suitable colour in the burned goods is often an essential property. Similarly, hardness is often of secondary consideration, but where resistance to abrasion is necessary, a hard material is usually essential.

The properties dealt with in this chapter are (*a*) colour ; (*b*) hardness ; (*c*) " feel " ; (*d*) " ring " ; (*e*) odour ; (*f*) taste ; and (*g*) sectility. The last three do not usually affect the working properties of the materials in any way.

COLOUR

The colour of an object is due to the fact that when rays of light fall on it some are absorbed, whilst others are reflected, the nature of the reflected light giving the surface a characteristic colour. Thus, objects which reflect red vibrations appear to be red in colour and so on. When the light is completely absorbed the object is *black*, whilst if the light is completely reflected without change the surface will be *white*.

Colour is exhibited in various ways, so that an object may show different colours under different conditions, viz. :—

1. The colour by reflected light.
2. The colour by transmitted light if the object is transparent.
3. The colour of the powder, as distinct from the mass (this is shown by drawing the mass along a piece of unglazed porcelain and examining the *streak* left on the latter).
4. The appearance of special types of colour, such as (*a*) *play of colours*, caused by the unequal bending of rays of light of different wave-lengths giving a vari-coloured effect ; (*b*) *opalescence*, which gives a pearly or milky appearance, as shown by opals ; (*c*) *iridescence*, or display of colours, due to inclusions of air or liquid in transparent crystals, or to peculiar irregularities in the surface of the material, as in some specimens of quartz, calcite, and mica ; and (*d*) *pleochroism*, a quality possessed by some transparent minerals, by which they exhibit different colours when viewed by polarised light passing through them in different directions (see also Chapter XV).

Lustre is a property which may be classed with colour ; it is due to the manner in which light is reflected from an object, rays of different wave-lengths being reflected at different angles and so producing diffraction effects. The lustre may be (*a*) *metallic lustre*, such as is exhibited by many metals ; (*b*) *vitreous* or *glassy*, as in glass, quartz, etc. ; (*c*) *resinous*, as in resin ; (*d*) *pearly*, as in pearls ; (*e*) *silky*, as in satin spar ; and (*f*) *adamantine*, as in diamond and some forms of carborundum.

Colour is a much more constant feature in opaque substances than in transparent ones ; the latter often vary greatly in colour, because of the presence of minute traces of other substances as impurities. Many substances have a characteristic colour, which is of value as indicating the nature of the material, *e.g.* iron, chromium, copper, uranium, etc.

The colours produced in transparent minerals are dealt with more fully in Chapter X on *Mineralogical Constitution* and Chapter XV on *Optical Properties*.

The colour of minerals varies considerably on account of (*a*) the presence of other materials and (*b*) the prior history of the material, including the effect of the weather. The surface of a material or article may change colour on exposure.

The colour of most raw ceramic materials is usually a minor property and chiefly of value as an indication of the impurities present. In finished articles, it is often a very desirable property and one which contributes greatly to their beauty. In some cases, the colour is more important than other properties, as in some ornamental ware and even in some utilitarian articles. Thus, an architect may select red bricks on account of their colour and may have to disregard the fact that the ones he chooses may not be as strong as some other bricks. It is often easy by firing bricks at a higher temperature to make them much stronger, but, if the colour is less pleasing, they will usually be difficult to sell. Fortunately, most bricks are so much stronger than is requisite for safety that the slight loss of strength which is incurred in order to produce a more pleasing tone or colour is quite negligible for most of the purposes for which such bricks are used.

The colour of a raw ceramic material does not necessarily give any indication either of its purity or the colour of the fired product. Consequently, such a material should seldom be judged solely on its colour. A dark-coloured material, such as some Devonshire ball clay, may be almost white when burned and its original colour will, in such a case, be no detriment to its usefulness. The same is true of most ceramic materials whose colour is due solely to the presence of carbonaceous matter which burns off in the kiln and is, in this way, removed and can do no harm. If the dark colour of the material is due to iron compounds—which are not removed by heating—it may completely spoil the material for some purposes. A light-coloured material, on the other hand, need not necessarily be of good quality, as it might contain a large proportion of colourless or light-coloured impurity, which would darken on heating or in other ways make the material unsuitable for some purposes.

Where a definite colour is desirable in the finished articles, it may be produced by various means such as :—

(*a*) By heating the material or articles at a suitable temperature, and in a suitable

atmosphere, so as to produce the desired colour. If the composition of the raw materials is suitable, no other treatment may be required. If certain colour-producing impurities are present in the raw material they may prevent the formation of the desired colour, in which case some other method must be employed. A typical example of this method of producing colour is a ferruginous clay, which, if burned at a certain temperature (depending on the clay) in an oxidising atmosphere, will produce a pleasant red colour, but if it is burned in a reducing atmosphere a dark, dull "blue" colour is obtained, whilst when reducing and oxidising atmospheres are used alternately in the kiln, a mottled or brindled appearance is produced.

(*b*) A coloured substance may be introduced into the raw material, so as to mask any undesirable colour and give the finished goods the desired tint. Thus, the addition of manganese dioxide will produce a dark brown or nearly black article, whilst cobalt compounds will give blue shades and chromium compounds green ones. The lighter the natural colour of the burned material, the greater will be the variety of colours which can be produced in this manner.

(*c*) If the colour of a fired material is undesirable it may be masked by coating the article with an engobe of another material which burns to a desirable colour. The engobes used for this purpose are usually white-burning clays or a mixture of such clays with flint, Cornish stone, or felspar, together with a suitable colouring agent if required, the engobe being adjusted so as to have the same shrinkage as the article to which it is applied, as well as the desired colour when burned.

The engobe is often covered with a transparent glaze, to protect it and render the article impervious to water. Sometimes, instead of a coloured engobe, a coloured glaze is used and in some faience and majolica ware a coloured glaze is used over a white engobe.

Where the colour is required to be in the form of a pattern, it may be applied direct to the article or to the engobe by means of a brush, stencil, transfer, or any other convenient method. If the ware is then covered with a glaze, the method is known as *underglaze* decoration. As such colours must not be adversely affected by the firing of the glaze, only a limited range of colours is available. If, on the other hand, the colours are applied to the article after it has been glazed and fired, a much larger range of colours is available. This method is known as *overglaze* decoration.

From the foregoing it will be seen that the most suitable method of obtaining any desired colour depends on the nature of the goods.

Natural Sources of Colour

A large number of the materials with which this volume deals are, when pure, perfectly white. Thus, china clay, magnesia, lime, alumina, zirconia, and silica, when quite free from impurities, burn to a perfectly white mass. Perfect whiteness is seldom attained on account of the presence of minute proportions of impurities, which have an appreciable influence on the colour of the material in which they occur. Thus, iron in small proportions is universal in its occurrence, and almost all

minerals contain at least traces of it. As iron compounds have a very pronounced colour when heated to redness (except in the presence of free lime, etc. (p. 102), iron is either a valuable accessory or a troublesome impurity, according to the conditions in which it occurs and the purpose for which the material is to be used.

The chief forms in which iron compounds occur in the *raw materials* are :—

(*a*) Free ferric oxide, Fe_2O_3.

(*b*) Free ferric hydroxide, $Fe_2O_3xH_2O$.

(*c*) Magnetic iron oxide, Fe_3O_4.

(*d*) Free ferrous oxide, FeO.

(*e*) Iron oxide combined with silica or with silica and alumina.

(*f*) Complex iron silicates or alumino-silicates. It was suggested by the author, in 1909, that a large proportion of the iron in some clays may occur as ferrosilicic acid, possibly equivalent to nontronite ($H_4Fe_2Si_2O_9$), which, on heating, is decomposed into water, silica, and free ferric oxide. This would account for the great change in colour which many clays undergo when heated, but, owing to the experimental difficulties involved, the correctness or otherwise of this supposition has never been proved.

(*g*) Iron (ferrous) carbonate, $FeCO_3$.

(*h*) Iron (ferric) sulphide, FeS_2.

(*i*) Iron (ferrous) phosphate, $Fe(PO_4)$.

For the mineralogy of the iron compounds, see Chapter X.

The colours produced by iron compounds are divisible into three classes : yellows, reds, and blues. In the raw state the colour of ferric compounds varies from pale yellow to reddish brown, according to the amount present in a clay or other material and the nature, size, and distribution of the individual particles. Ferrous compounds impart a bluish or greenish tinge, which is often less noticeable than the more pronounced colour of ferric compounds. Various modifications of the above-mentioned colours also occur, some iron compounds imparting a grey colour to the material in the raw state. Thus, most fireclays and some sandstones are grey, owing to the presence of ferrous carbonate or finely-divided iron pyrites, or, in rare cases, to iron phosphate.

Ferrous sulphate is a very troublesome impurity in clay, as it cannot easily be removed by washing, and, unless converted into an insoluble material, it often produces a bluish-green scum on the surface of the dry but unfired articles. If necessary, it can be avoided by adding a little barium carbonate to the clay, so as to convert the iron salt into insoluble ferrous carbonate and barium sulphate.

Red and Yellows.—Some raw ceramic materials, such as bauxite, magnesite, breunnerite, laterite, and some clays, are yellowish or reddish in colour. This is commonly attributed to limonite and to hæmatite. The former is yellow, and the latter yellow to red, according to the state of oxidation, combination with water, and state of subdivision. They consequently impart a corresponding tint to any material in which they occur, subject to the proportion present and the influences which tend to prevent their characteristic colour being produced.[1] Ferrous and

[1] It is said that there are some red clays whose colour is due to the presence of algæ. The colour of such clays is deeper in the raw than in the fired state.

ferric oxide, either free or in combination with water or other substances, are the source of a large range of colours, varying from the lightest tawny yellow, through full yellow, orange, to a rich red colour, which resembles that so much desired in facing bricks.

In the fired or burned ware, the number of iron compounds is usually less than in the raw materials, because the hydroxides, carbonates, sulphates, sulphides, and phosphates are usually decomposed in the kiln, yielding one or more of the oxides or complex silicates. When heated to bright redness, under oxidising conditions, most iron compounds impart a reddish colour to the clay or other material containing them. This colour is commonly regarded as due to the conversion of the iron into ferric oxide, though other complex compounds are probably present, as the material is not bleached by boiling it with hydrochloric acid, which would dissolve ferric oxide.

The colour of raw clay may be partly destroyed by hydrochloric acid, but all the iron cannot be removed, either from the raw or fired clay. This would seem to support the idea that the iron is combined in some way with silica, or with silica and alumina, unless it is converted into a dense form of ferric oxide, which is soluble only with great difficulty in hydrochloric acid.

The colour produced by ferric oxide in fired ware is extremely variable, as it depends upon so many factors ; for this reason, the colour produced by iron compounds naturally present in the raw materials cannot usually be matched by adding any prepared materials.

Seger considered that the colour developed by iron compounds in an oxidising atmosphere depends on :—

1. The amount of iron oxide or its equivalent present and the nature of the compound.
2. The composition of the fire-gases during the burning.
3. The temperature at which the material is burned.
4. The amount of other constituents.
5. The amount of vitrification which occurs.

It will usually be found that (when other conditions are constant) the colour is, to some extent, dependent on the proportion of iron present if it is in a sufficiently finely-divided condition. Thus, the presence of the equivalent of 4 per cent. of ferric oxide [1] in a clay will usually impart a good deep-red colour to the burned clay. With only 3–4 per cent. the colour is more usually brown or purple, whilst with less than 3 per cent. the colour varies from deep buff to nearly white, the depth of colour diminishing with a decrease in the proportion of iron oxide present. It is, however, almost impossible to predict the colour of a burned clay from the proportion of ferric oxide, as there are so many other factors involved, such as the size of the particles and their previous history. In fact, Orton is very emphatic in expressing the opinion that the colour (when fired) of a red-burning clay bears no relation to its iron

[1] It is customary to refer to the iron compounds in clays, etc., as though they were all present as ferric oxide. Actually, several compounds may be present, so that the term " ferric oxide " must be understood to mean the equivalent and not as necessarily implying that all the iron is in the form of ferric oxide.

content, as many clays burn to the same colour, no matter whether they contain 4 or 8 per cent. of ferric oxide. He further remarks that " the distribution seems more important than the amount " and " the conditions of firing exercise a still greater influence, so that, whilst clays low in iron never burn red, it is not possible to estimate the colour of the fired ware from the proportion of iron present."

If a buff-coloured brick is examined under a microscope it will be seen to consist of different-coloured materials, in the form of tiny patches or dots, the colours varying from white or the yellow tint of the fired clay to brown, red, or even black spots. To the naked eye these all blend together, giving a uniform buff colour, and the more abundant the dark spots, and the nearer they are together, the deeper will be the colour ; *i.e.* the larger the proportion of effective iron compounds present, the deeper will be the colour. The effect is similar to that produced by a large number of coloured dots on a white sheet of paper. When the sheet is held at a distance the whole surface appears to have a uniform tint. This uniformity of colour is only attained when the particles are extremely minute and very regularly distributed, and from this comparison it will readily be understood that the colour of a piece of fired material does not depend only on the proportion of iron compounds present, but also on the size of the particles and on the manner in which they are disseminated through the mass.

The effect of the size of the grains of iron compounds is well shown in the following : (*a*) If a piece of clay is soaked in a solution of a soluble iron salt, dried rapidly and burned, it will have a strong red colour ; (*b*) if another sample of the same clay in the form of a cream or slip is mixed with a soluble iron salt, and the latter is afterwards precipitated by ammonia, and the clay is evaporated to dryness, dried and burned, it will also have a dark-red colour ; (*c*) if powdered hæmatite ore is mixed with another sample of the same clay, which is then fired as before, a brownish-red colour is produced ; whilst (*d*) if the iron oxide were in a still coarser form, the burned mixture, as a whole, would be only slightly coloured, but it would have red blotches and spots. In all these cases, the total amount of iron is the same, the difference in colour in each case being due to its form and distribution.

When a solution of an iron salt is used it permeates the whole mass and the iron is disseminated throughout the clay uniformly, except in so far as some of the solution is drawn to the surface by capillary attraction. The powdered ore is less thoroughly mixed, and, therefore, gives a less intense colour, whilst the larger grains of material merely produce spots, the remainder of the clay being scarcely coloured. It will thus be seen that to produce the characteristic colour of red-burning clays the iron compounds present must be in an extremely fine state of division and uniformly disseminated throughout the whole mass. Coarse particles merely impart a colour to a comparatively narrow zone around them, whilst the rest of the mass is unaffected. For this reason, the colour of clays cannot materially be improved by the addition of artificially prepared iron oxide, as the latter is far too coarse to give a homogeneous tint to the clay.

The iron compound in red-burning clays is in so impalpable a state, and is disseminated through the mass to such an extent, that it is almost impossible to attain a

similar material by artificial means. The nearest approach to it is to add a solution of a soluble iron salt to the clay, but unless special precautions are taken (which usually result in segregating the iron and so spoiling the effect) the solution tends to accumulate on the surface of the articles during the drying stage and is brushed or rubbed off when handling the goods. In the United States, a superficial red colour is sometimes imparted to terra-cotta by spraying the dried, but unfired, ware with a 20 per cent. solution of ferric chloride and afterwards firing the ware in the usual manner. A solution of ferrous sulphate appears to be useless for this purpose.

The colour produced by iron compounds on the fired ware is also greatly influenced by the conditions under which it is burned. Comparatively small changes in the composition of the fire-gases and of the atmosphere in the kiln make a great difference in the colour of the ware. The best and most brilliant red is obtained by heating the goods slowly in an atmosphere containing a large excess of free oxygen, taking care to avoid the temperature rising so rapidly that any carbonaceous matter in the clay can reduce any ferric compounds present. To some extent, the effect of a temporary reducing atmosphere may be overcome by later careful oxidation, but the resultant colour is seldom so good as if the conditions had been entirely oxidising throughout the whole period of firing. It is especially important that between 700° and 900° C. the atmosphere of the kiln should be highly oxidising, so that any of the lower forms of iron oxide may be oxidised to ferric oxide before the temperature at which they commence to fuse is attained. When once the fusion of some of the ferrous compounds has occurred it is almost impossible to re-oxidise them so completely as to obtain a pure red colour.

The temperature to which the goods are heated is also of importance in the development of the red colour of ferric oxide ; the colour produced on firing a red-burning clay becomes brighter and lighter as the temperature increases, until a maximum brilliancy is attained, usually at a temperature equivalent to Seger Cone 1a (1100° C.). At higher temperatures, partial fusion takes place and the colour is gradually darkened, the red being replaced by brown. The temperature at which the red colour is perfected depends upon the clay and varies with different materials. Some clays assume a brilliant " terra-cotta " red colour when merely baked at 900°–1000° C., whilst others scarcely develop any red colour at such temperatures.

It has been frequently stated that ' such and such ' a temperature will form a red brick and that a higher temperature will form a blue one. This is only true when other conditions are satisfied. Thus, a clay practically free from iron will not produce a red colour at any temperature unless iron oxide be added to it, and many clays which will produce a good red brick will not form a satisfactory blue one, because they either do not contain sufficient iron or because they will not stand heating to, and reduction at, the necessary temperature. Hence, the principle that the temperature regulates the colour is only true within limits ; beyond these the statement does not apply.

As a general rule, the red colour begins to be replaced by brown as soon as an appreciable amount of fused or vitrified material is formed ; the iron oxide then appears to combine with other minerals, yet it has never been satisfactorily

explained why free ferric oxide (to which the red colour is generally considered to be due) can remain uncombined with the silica of the clay for so long at temperatures above 900° C. It may be due to the clay remaining unvitrified, and, therefore, practically inert, but this explanation cannot always apply, because the red colour is retained to perfection in a few clays which have been fully vitrified. As Orton says, "It is truly hard to see how iron oxide can be wholly free and uncombined in a vitrified mass of such perfection," though it appears to be so, and the fact that, on further heating, these clays blacken and iron silicates are then formed, makes it appear probable that the combination of the iron compounds with the silica of the clay can only result in the loss of their red colour and in the production of black (technically "blue") wares due to the formation of ferrous silicates. Whether the true explanation of the inertness of the so-called free ferric oxide in red-burning bricks will ever be explained is a problem which only the future can solve.

Effect of Minerals on Red Colour.—The presence of various materials in a clay has an important influence on the colour developed by iron compounds. If a large proportion of colourless matter, such as sand, etc., is present, especially if it is somewhat coarse, the colour developed by the iron compounds is not so intense as might be expected from the percentage of iron oxide shown by analysis. The difference may be partly due to adsorption phenomena (see Chapter VI), as the colouring matter cannot so readily tint grains of sand and other impervious minerals as those of the more porous clay.

The red colour produced by iron compounds is also modified by free alumina, Seger having found the following relations between the composition and colour in various clays :—

Character of clay.	Colour after burning.
High in alumina and low in iron . .	White, or nearly so.
High in alumina and moderate in iron .	Pale yellow to pale buff.
Low in alumina and high in iron . .	Red.
Low in alumina and high in iron and lime .	Cream or yellow.

According to Seger, some clays containing iron compounds have, when burned, a yellowish colour due to the interaction between the iron compounds and the alumina, the latter decolorising the iron in the same way as lime (p. 102), though to a much smaller extent, as lime is a more powerful base. His experiments suggest that the best red-burning clays contain two or three times as much alumina as iron oxide. This influence of alumina is not admitted by Orton,[1] who denies the bleaching action of alumina upon iron oxide, because he has found buff-burning clays of practically the same colour, the composition of which fluctuates between 40 per cent. of alumina and 0·5 per cent. of iron oxide, and 15 per cent. of alumina and 2·5 per cent. of iron oxide. L. A. Keane,[2] on the contrary, has found that alumina sometimes aids in the distribution of the iron oxide through the mass by peptisation and also prevents the proper formation of the red colour by ferric oxide.

[1] *Trans. Amer. Cer. Soc.*, **5**, 389 (1903). [2] *J. Phys. Chem.*, **20**, 724–760 (1916).

The presence of some other oxides, such as *lime*, *magnesia*, and *alkalies*, is also adverse to the production of a good red colour by iron compounds, as they tend to cause the clay to fuse and so darken the red colour and form an unpleasant shade of brown. This is supposed to be due to the iron oxide combining with the fused material forming iron silicates, which do not possess the red colour of the free ferric oxide, but see p. 98.

Lime, when present in a red-burning clay, will combine with the iron present to form a white or cream-coloured double silicate. The white Suffolk bricks are produced by this means. Seger has found that the whitest products are obtained when the proportion of lime is equal to not less than two and preferably four times that of the iron expressed as ferric oxide. In practice, a large proportion of lime or chalk is usually necessary.

The decolorising effect of lime cannot occur when sufficient sulphurous fumes are present in the kiln gases, as these combine more readily with the lime than the iron does and form calcium sulphate, which produces a scum on the surface of the goods. The inside of the articles, however, which are not affected by the sulphurous gases, are decolorised in the normal manner. This effect of sulphurous gases is well shown by some tests made by Aron, who found that the red parts of bricks contained 8·49 per cent. of sulphuric acid, whilst the decolorised parts contained only 0·6 per cent.

Maw has found that the presence of 5 per cent. of *magnesia* prevented the production of the red colour in various clays which he examined.

Lime and magnesia each neutralise the colour of iron compounds to the extent of about half their weight, so that a clay containing 4 per cent. of iron oxide and 6 per cent of magnesia or lime will, when burned, have a colour such as would be produced were lime and magnesia absent and only 1 per cent. of iron oxide were present.

The effect of *fine fluxes* in destroying the red colour produced by iron is shown by the fact that coarse, sandy clays retain their red colour when heated to a higher temperature than fine-grained clays, as the latter contain a larger proportion of fluxes which fuse at a lower temperature and so cause the loss of colour (due to the formation of iron silicates) at a lower temperature than would otherwise be the case. Thus, E. Orton found that a sandy clay retained a strong red colour up to Cone 8, but another red-burning clay containing a larger proportion of actual clay attained a maximum red colour at about Cone 1. Above this temperature, the colour became dark brown and was spoilt by the formation of silicates. Ries has also confirmed this effect of fluxes.

The red colour is best produced in the absence of all other impurities than iron oxide and this should occur in an extremely finely divided condition, disseminated uniformly through the clay. If necessary, the clay may be purified (Chapter VI) so as to improve the red colour produced by the iron oxide present.

Blues and Blacks.—The blue or black produced in fired goods is usually due to the presence of ferric sulphide, ferrous compounds, or to magnetic iron oxide, each of which can combine with silica at a red heat to form a dark, fusible, slag-like mass, which is readily absorbed by the porous, fired clay to which it imparts its colour.

Ferric sulphide (pyrites) produces isolated black spots in the fired ware. These are due to the ferric sulphide (FeS_2) losing half its sulphur at a temperature of about 800° C. and to the resulting ferrous sulphide (FeS) combining with any free silica present and forming a dark fusible ferrous silicate. If the particles of sulphide are very small, they produce isolated black spots, but if they are larger or very numerous they form blotches or patches of a dark slag-like material which may be ½ inch or more in diameter and render the ware unsightly.

The iron in fireclays appears to be largely in the form of pyrites, and those clays are consequently buff or light yellow when burned, with small spots or patches of dark slag disseminated through the mass in proportion to the amount present. Pyrites never occurs in such fine grains as to give an even red colour to the goods in which it occurs, but usually produces dark spots in the ware.

Magnetic oxide of iron (Fe_3O_4) is black and is produced by the partial reduction of ferric oxide, under conditions which do not permit its complete reduction to ferrous oxide. It occurs in some raw clays and in some buff bricks, in the firing of which there has been a slight reducing action. It is similar in action to a mixture of ferrous and ferric oxides.

The *ferrous compound* naturally occurring in raw ceramic materials is chiefly ferrous carbonate, with small proportions of ferrous hydroxide or oxide. When heated in the absence of air, all these substances form ferrous oxide (FeO), and may, without serious risk of error, be considered as though they consisted wholly of ferrous oxide.

When a material containing ferric sulphide (pyrites, FeS_2) is heated, it parts with half its sulphur, forming ferrous sulphide, which rapidly combines with any free silica present and this also behaves like ferrous oxide.

Ferrous carbonate is often difficult to oxidise, even in a suitable atmosphere, and so does not always give a good red colour. It has a tendency to granulate and to produce black or dark brown spots, but if the clay is finely ground and the kiln is skilfully managed a fairly good red colour may be produced.

Ferrous oxide is the lowest oxide of iron and has a bluish colour. It does not usually occur in the free state, but is produced in firing under reducing conditions, and then, on account of its low fusing point, it readily combines with silica, forming fusible ferrous silicates, which produce a blue or blue-black colour in the fired goods. The conditions under which ferrous oxide is produced are determined by the nature of the clay, the proportion of iron compounds present and the manner in which the clay is heated. The ferrous oxide probably exists as such for only a few moments ; it either combines almost immediately with any adjacent clay or silica, or if this is impossible it usually becomes oxidised to ferric oxide during the cooling of the material in the kiln.

Ferrous oxide is produced by the reduction of red ferric oxide by carbon monoxide and other reducing agents in the gases used for heating the material. If the reduced oxide is sufficiently abundant and properly distributed it forms a ferrous silicate and so produces the dark fusible material to which Staffordshire blue bricks owe their characteristic appearance. The reduction process is known as " blueing " ; it may

be produced intentionally in a variety of ways, in some of which the use of free carbon, hydrocarbon, carbon monoxide, or possibly hydrogen, is required. This free carbon, carbon monoxide or hydrogen may be produced by the gases from the coal used in heating the kilns, or by the use of heavy residuum tar, juniper wood or other hydrocarbons. By whatever means either is produced, its action is to reduce the iron compounds present in the clay from the ferric to the ferrous state, in which they can combine readily with the silica and heated clay, forming complex silicates of a slag-like character. These molten slags rapidly fill the pores of the material, so that when the "blueing" is complete the mass is no longer porous, but consists of a vitreous material, the pores of which have been completely filled with a tough glass or slag, the whole forming a solid mass of great strength and toughness.

The manner in which the reduction takes place does not seem capable of any simple expression, but apparently the first stage consists in the production of magnetic oxide and this is later reduced to ferrous oxide or silicate, or possibly iron carbide (Fe_3C) or carbonyl ($FeCO$) may be formed, at any rate in part, a considerable amount of free carbon being also deposited in the pores of the clay when oils, or certain special materials, are used to produce the blueing. The action of these reducing agents may be represented by four equations :—

Fe_2O_3	+	CO	=	$2FeO$	+	CO_2
red		gas		black		gas
Fe_2O_3	+	H_2	=	$2FeO$	+	H_2O
red		gas		black		water vapour
Fe_2O_3	+	C	=	$2FeO$	+	CO
red		"smoke"		black		gas
$3Fe_2O_3$	+	C	=	$2Fe_3C$	+	$9CO$
red		"smoke"		iron carbide		gas

Under the usual conditions of working, the gases which effect the burning contain about 25 per cent. of carbon monoxide, and if there is insufficient air to burn the gas to carbon dioxide, the burning gases will draw supplies of oxygen from the higher compounds of iron in the goods, thus converting them into the lower or ferrous state.

In order to effect the complete blueing of bricks or tiles, the gas should be as clean as possible, as if it is charged with large quantities of soot the outside pores may be filled with deposited material which prevents the interior of the goods from being properly blued and the latter, if broken, will not be "blue throughout." The articles must also be sufficiently porous to allow the reducing gases to enter and effect the reduction.

Another reaction which may aid in the blueing is the formation of magnetic oxide of iron by the partial reduction of red ferric oxide (p. 103) and the subsequent dissociation of this into ferric and ferrous oxides. At a sufficiently high temperature, ferric oxide can also dissociate, evolving atoms of oxygen from its molecules and forming the magnetic oxide

$$6Fe_2O_3 = 4Fe_3O_4 + O_2.$$

The blueing is usually effected by the reduction of the ferric oxide, but if this fails

the kiln may be heated more intensely with as little admission of air as possible, in order to decompose any remaining red ferric oxide and convert it into the black magnetic oxide which subsequently decomposes and forms fusible silicate.

Some of the magnetic oxide may also remain in the free state, in which case, as it is black, it adds to the dark colour desired.

Although the process of blueing may be explained as due solely to the reduction of ferric compounds in the clay, such an explanation cannot be complete, because the colours of synthetic ferrous silicates are quite different from that produced in bricks by firing in a reducing atmosphere; the latter are probably coloured by carbonaceous matter (from the smoke produced by the fuel) as well as by the ferrous silicates, though carbonaceous matter alone, in the absence of iron, produces black, but not " blue " ware. If the temperature at which the blueing has been effected is not too high, the red colour of the ware can be restored by reburning in an oxidising atmosphere; this reversal of colour may be repeated indefinitely if the temperature is carefully controlled and seems to suggest that the iron in blue bricks may be combined with some form or forms of alumino-silicate, in which its state may readily be changed from ferrous to ferric, or *vice versa*. On heating to higher temperatures, however, this compound (?) appears to be decomposed and irreversible silicates are formed.

The effect of the size and distribution of the particles of ferrous iron compounds appears to be as important as in the production of a red colour by ferric compounds (p. 99). A uniform " blue " colour is only produced when the iron compounds are in an extremely fine state of division and are uniformly disseminated through the material. When they occur in large pieces they form blotches of a blue-black material similar to those produced by coarse particles of ferric sulphide (pyrites) (p. 103).

The effect of impurities in the clay (other than iron compounds) in the production of a " blue " colour has not been adequately studied, but so far as can be ascertained, lime, magnesia, and the alkalies do not affect the production of a blue colour unless present in such large proportions as to render the clay too fusible to enable it to keep its shape at the temperature required for blueing.

Black ware and the black discoloration and cores are usually produced by ferrous and magnetic oxides, either alone or with unburnt carbon and are due to a deficiency of air when the goods are at a temperature between 500° and 900° C., particularly if the temperature rises very rapidly, so that the carbonaceous matter is not burned out before vitrification commences at the surface of the goods and prevents the proper oxidation of the carbonaceous matter in the interior. Such a state of affairs is due to unskilled management of the kiln and is considered fully in the author's *Clayworkers' Handbook* (Griffin).

The colours produced by iron compounds do not always belong to one or other of the three classes mentioned on p. 97. In some cases, mixtures of different colours are obtained. Thus, if a clay containing sufficient iron oxide is burned in an atmosphere which is alternately oxidising and reducing, such as may be caused by the presence of an excess of air at some periods in the burning and a deficiency of air

at other periods, a variegated colour or " brindled " effect may be produced. In the oxidising atmosphere, the iron compounds produce a red colour, but when the atmosphere becomes reducing a part of the iron compounds may be changed into the ferrous state, this giving a blue colour. If the alterations are fairly rapid, the reduction or oxidation cannot be completed so that the resultant products contain some iron compounds in the reduced and some in the fully oxidised condition, thus producing a mottled appearance. When this effect is produced deliberately, it is known as " flashing " ; it is frequently employed in the production of certain classes of facing bricks and other goods and with small kilns worked at moderate temperatures it is not difficult to obtain very pleasing effects. The difficulties increase rapidly, however, with an increase in the temperature and size of the kilns. The great point is to secure the complete oxidation of the carbon in the clay (if any be present) at a sufficiently low temperature, so that it cannot combine and reduce the iron in the clay to such an extent that subsequent oxidation becomes impossible. Too rapid heating of the kiln when it is just below 900° C. is also the cause of thousands of facing bricks being spoiled, because the carbonaceous matter they contain is decomposed and " set " in such a way that it cannot afterwards be burnt out without spoiling the colour of the goods. Whilst this process of flashing is often intentional, to secure certain effects, it sometimes occurs when it is not wanted and is then regarded as a defect. In such cases, it is generally due to lack of skill in firing the kiln and especially to putting the fuel in the firebox in too large quantities at too long intervals, instead of smaller charges supplied more frequently.

Carbonaceous Matter.—Next to iron, probably the most important colouring agent in raw materials is carbonaceous matter.

The grey, bluish black, red, and other tints of unburned clay and other minerals, although usually due to mineral impurities, are, in some cases, of vegetable origin, the composition of the colouring matters being often imperfectly understood. It is not improbable that it is partly due to finely-divided coal, or to some dye-like material formed—like the brown colouring matter of peat—by the decomposition of vegetable matter.

These organic colouring matters are destroyed on firing, so that a clay may be strongly coloured in the raw state and yet burn perfectly white.

Ball clays are typical examples of materials containing a large amount of organic colouring matter. Some of them are dark blue or even black, but when heated to redness in an oxidising atmosphere they become almost white or pale buff, according to the other impurities present. Most natural clays, and many refractory materials, are coloured to some extent by carbonaceous matter. Further information on the colouring effect of carbonaceous matter will be found in Chapter X.

Use is sometimes made of the fact that carbonaceous matter burns out in the firing, by mixing special bodies and pastes with some strong aniline dye, such as methylene blue, which will burn off in the kiln, but which imparts a distinctive colour to the material whilst in the raw or dried condition, but which does not affect the fired goods. By this means, the unfired bodies may be identified by the colour.

Colours of Raw Clays

The colour of a raw material is no criterion as to its colour when burned. A clay which is grey or yellow when freshly dug may, on burning, give a good red colour, equally as well as a clay which is a red or brown when first found. This is largely due to the fact that the colours of natural clays is largely organic in character and so is destroyed when the clays are heated. It is also due to the fact that the iron compounds in clays are usually very pale in colour, or are almost colourless and only develop their full red or blue colour when the clays are fired.

The two principal colouring materials in clays in the raw state are iron oxide and carbonaceous matter (pp. 97 and 106).

Variations in colour in different strata do not necessarily indicate any appreciable difference in composition, nor is the colour of a deposit necessarily a reliable guide to the purity of the material, as the amount of impurity producing a certain colour may be very small in comparison with the colour it produces.

The colour of a ceramic material may vary in different parts of the same bed on account of its proximity to other strata, or for other reasons. Thus, if a clay bed lies immediately below lignite, the portion in contact with the carbonaceous bed may be bleached by the reduction of the iron compounds, whilst the lower portion of the clay bed may be quite dark in colour.

The exposed surface of light-coloured beds is sometimes brown, as a result of the oxidation of the iron compounds in the clay, and if a section is examined it may be found that the colour gradually becomes lighter and lighter, with increasing depth. The extent of coloration by oxidation is largely dependent upon the permeability of the material. Thus, an open material would be stained to a greater extent than a close-grained one, whilst the presence or absence of fissures and cracks would also affect the resultant colour.

Very few clays are pure white when in the raw state, as the presence of only a very minute proportion of impurity may affect the colour to a considerable degree.

Kaolin and **china clay,** when reasonably pure, should be white or pale cream in colour, but the tint varies irregularly with the amount of impurity present. Some less pure primary clays have a greyish tint on account of carbonaceous matter present, whilst others are slightly brown as a result of the presence of small proportions of peat or iron compounds. Some china clays are tinted pale blue on account of bright blue needle-shaped crystals of tourmaline present in them. China clay varies in whiteness to a considerable extent, according to the amount of moisture it contains. If a sample is dipped in water it may become grey or bluish in colour ; some china clays when so treated have a distinct yellow tint, though they are practically pure white when dry.

Ball clays may be black, blue, brown, or white. The black is due to the presence of carbonaceous matter, some ball clays containing as much as 10 per cent. of carbon in the form of lignite or other organic matter. Many ball clays contain 3–4 per cent. of carbon, which is equivalent to a much larger proportion of carbonaceous matter.

Some of the purest varieties of ball clays in S. Devon are white, but the variety

known as " white clay " varies in colour from snow white to a pale straw tint. Other ball clays vary in colour in different beds, through grey, blue, brown, or chocolate colour to a deep black. The colours of the Dorset ball clays are equally variable. In each case, the greater part of the colour is due to carbonaceous matter, though some clays are tinted with iron oxide and hydroxide. If this is separated by a washing process, it usually produces a good quality of ochre.

Many of the so-called " blue " ball clays (including some of the best kinds of ball clays) are yellowish or grey in colour when freshly obtained, but when exposed for some time they become tinged with brown, though even after prolonged exposure they do not become much darker in colour and sometimes they turn rather paler. Some blue ball clays are spotted or mottled, but this does not affect their colour when burned.

Ivory ball clays are creamy, drab or blue-grey in colour and are very similar to blue ball clays except that they contain more iron. When exposed to the weather, ivory ball clays differ from the blue variety in becoming " rusty," due to the oxidation of the iron salts present.

Surface clays and **brick earths** are very variable in colour according to the impurities they contain. The commonest are yellow, brown, and blue ; these colours are due to the presence of iron compounds. Thus, a yellow colour in clays may be due to the presence of ferric hydroxide (limonite, $Fe_2(OH)_6$) or to the colour of the iron being rendered paler by the action of lime compounds disseminated through the clay (p. 102). The green colour of some raw clays may be due to the presence of iron silicates, such as glauconite.

Many stoneware clays, when freshly dug, are grey, yellowish, or blue, the blue shade being due partly to the presence of ferrous compounds. Silt, warp, and similar beds are often of a light chocolate colour. The pocket clays of Derbyshire and Staffordshire vary very considerably in colour. Some are quite white, whilst others are yellow, red, purple, mottled, and even black. The whitest of these clays are not necessarily the purest, but owe their appearance to the presence of minute flakes of mica which make the material white and glistening.

Fireclays and some **shales** are a grey or slightly bluish colour on account of the presence of organic matter which occurs in minute particles disseminated through them. Some fireclays are quite black and have bright cleavage faces. Near the surface, a clay may be nearly white with a slight tinge or mottling of red, grey, or yellow, but patches of strongly ochre-coloured material often occur at a slightly greater depth. Some shales, after being dug and exposed to the action of the weather, turn yellow or brown as a result of the oxidation of the iron compounds present.

Some clays are naturally mottled on account of the irregular distribution of impurities in them ; the " mottling " usually disappears during the firing.

Colours of Burned Clays

As previously explained, the colour of a burned material, and particularly of a burned clay, has no constant connection with its colour before firing, though in some cases it is possible to predict roughly what will be the colour.

The colour of burned clay depends chiefly, but not wholly, on the proportion of iron present. Clays which contain only a very small proportion of iron will be white or pale cream when fired, and, as the proportion of iron oxide increases, the colour will vary from primrose yellow through buff, red, brown, grey, blue, or black, whilst in some cases, it may be mottled on account of the irregular distribution of the iron compounds present.

Table XXI shows the colours which may be expected from clays of various colours in the raw state, though, as already explained, it is impossible to predict the colour with certainty.

TABLE XXI.—*Colour of Burned Clay*

Colour of Raw Clay.	Probable Colour of Burned Clay.
Red	Red.
Deep yellow	Buff or red.
Chocolate	Red or reddish brown.
White	White or yellowish white.
Grey or black	Red buff or white.
Green	Red.
Red, yellow, or grey (calcareous)	Red at first, then cream yellow, buff, or white, and then greenish yellow when becoming viscous.

Kaolin and **china clay,** when pure, are perfectly white after burning; if they contain a very minute proportion of iron compounds, the burned clay has a pinkish or reddish tinge. For some purposes, a slight discoloration is not of great importance, as it does not appreciably affect the refractoriness.

Ball clays are white or cream in colour when burned. Ivory ball clays generally become a yellowish buff when burned, as they contain a larger proportion of iron oxide than the purer varieties of ball clay.

Brick earths, when burned, vary considerably in colour, according to the conditions mentioned on p. 96. *Red-burning clays* owe their colour to the presence of iron compounds and the absence of more than very small proportions of other impurities. Some of these clays are renowned for the beautiful red colour which they assume when burned. Amongst these are the Ruabon clay, the "red marls" of Staffordshire and Leicestershire, and the red-burning clays of Shropshire, Lancashire, and North Wales.

Other good red-burning clays occur in Hampshire, Berkshire, Nottinghamshire, Leicestershire, Lancashire, and Yorkshire. Good colours may be obtained with many other clays, but the ones mentioned are usually the most pleasing.

Bagshot clays are well known for the excellent red colour they produce, whilst

the Oxford clays are somewhat lighter. The Midland and Western clays give varying shades, most of them burning to a red colour. The majority of surface clays are red when fired, though there are some exceptions. Many shales burn to a red colour, though others are much lighter when fired.

The value of some red-burning clays is dependent on the absence of scum, specks, blisters, etc., which sometimes accompany and spoil what would otherwise be a good colour. Black, white, or cane-coloured spots also occur and spoil the appearance of some red-burning clays. The best clays give a good red of uniform character over the whole brick, but some architects and builders prefer bricks, etc., with an irregular, spotted or mottled appearance due to the presence of iron compounds in a coarser state than that which produces bricks of a uniform red tone. Thus, some of the Humber silt produces bricks of very variable colour, all shades from dark purple to dirty white, though blue, red, and yellow are sometimes found in the same brick. When these varied colours form a pleasing combination the clays may be valuable, but, as the tints cannot usually be regulated, the risk of producing unsaleable goods is often very great. Facing bricks, terra-cotta, floor tiles, roofing tiles and some coarse pottery are dependent on the production of a pleasing red colour when fired at a moderate temperature and the value of the clays used for making these articles depends on the quality of the red colour produced. If too high a temperature is required to develop the colour, the production of the goods will be costly and in most cases, the colour will not be very pleasing.

E. Orton [1] has stated that a good red-burning clay should have a yellow, red, or salmon colour at 900° C. and should attain maximum brilliance at about 1100° C. Many of the bricks and tiles of the Midlands and North of England are usually burned at a higher temperature than is required to produce the most pleasing tint; this is done to secure increased strength and a less permeable product which will remain "clean" longer than a very porous brick. W. G. Worcester [2] has stated that a good roofing tile clay should give the following colours at the temperatures shown in Table XXII:—

TABLE XXII.—*Colour of Roofing Tiles*

Colour.	Cone.	Temperature, ° C.
Immature and high red colours . . .	Up to 06a	Up to 980
Commercial red	05a–1a	1000–1100
Overmature red or brown with body still sound	2a–4a	1120–1160
Blue or black colours with failure of body .	5a and over	1180 and over

Many manufacturers, unfortunately, place the colour of their goods before anything else and will even sacrifice durability in order to obtain a certain "saleable

[1] *Trans. Amer. Cer. Soc.*, **5**, 413–415 (1903). [2] *Geol. Survey of Ohio, Bull.* **11**, p. 102.

tint." There is much excuse for their doing so when there is a ready demand for their goods, but it is unfortunate all the same. The result of this is that many bricks have been very imperfectly "baked" in the kiln, the heat being merely sufficient to develop the required colour and no more. Such bricks may last a long time under favourable circumstances, but they cannot compare for durability with those which have been heated to the point of incipient vitrification, where the particles of clay are bound together by the molten particles of the more fusible constituents of clay.

Blue and black bricks and tiles are usually formed by burning clays containing a sufficient proportion of iron compounds in a reducing atmosphere (p. 102), though they may also be due to the presence of manganese dioxide occurring naturally in a clay or added thereto.

Black bricks are sometimes produced by the deposition of carbon in the pores of articles, the particles being subsequently fixed by the fusible matter on the surface of the goods. Crucibles, etc., composed of a mixture of clay and graphite are also black.

A purple colour on bricks and tiles is sometimes a result of the partial reduction or of the decomposition by overheating of red ferric oxide in the clay. Some clays yield this colour more readily than others, but it can sometimes be produced by adding a little manganese dioxide, coke-dust, or even ashes, to a clay, though no artificial mixture is quite reliable. It is usually found that only a small proportion of the goods fired in a kiln possess the desired purple colour ; the others may be blue, brindled, or red.

A mottled or irregular colour may be due partly to the composition of the material and partly to the method of firing. With materials containing much combustible matter—whether in the form of cinders added under the name of "soil," or of material naturally present as "organic vegetable matter" or "shale oil"—a certain amount of irregularity of colour is practically unavoidable unless the means used to mix the material are so complete and the combustible matter is so fine, that a perfect distribution can be effected. In most cases, in the parts of the goods where the combustible matter is most prevalent, it will burn without a sufficient quantity of air and will consequently take the oxygen from any iron compound in the immediate vicinity, provided that such oxygen is available. This will necessarily lead to a change of colour in certain portions of the goods, for the reduced iron compound will be bluish or even black, whilst the fully oxidised one is red. This kind of irregularity in colouring can only be avoided by so fine a grinding and so thorough a distribution of the combustible matter as is quite unattainable in commerce, and it is a fortunate thing that many of the irregular colours produced are so effective when the bricks, tiles, etc., are in use, that they are actually sought for by architects and others.

In the absence of sufficient combustible matter in the goods, a mottled or irregular appearance may be produced by alternate reducing and oxidising atmospheres in the kiln. By repeatedly changing the nature of the atmosphere the iron compounds are partly reduced and partly oxidised, this giving a mottled or flashed appearance which is highly prized in goods made for some purposes (p. 106).

The speckled bricks so valued in America are made of light yellow clays containing

manganese dioxide, which causes small black spots to appear on the surface of the bricks.

Further information on mottling and variegated colours will be found on p. 106.

Whiteware.—The term " white " is often used very loosely in clayworking, and is used to include all shades from a true white to a distinct cream or even a pale yellow colour.

White goods, when made of clay, are usually formed of white-burning clays, etc., of great purity, or of a mixture of china clay, ball clay, flint, Cornish stone, felspar, etc. When such clays or mixtures are too costly to be used to form the whole article, the latter may be made of a cheaper clay which is buff or red when burned, but is made to appear white by covering it with a white-burning mixture, such as that just mentioned. This process is known as engobing or bodying (p. 96).

Some clays containing a large amount of calcium carbonate, as well as a considerable proportion of iron compounds, are quite white when burned. They are used for making white bricks in Cambridgeshire, Norfolk, and Suffolk and to a smaller extent in Sussex. They owe their whiteness to the combination of the iron with the lime, silica, and alumina in the clay.

Gault clays (which sometimes contain as much as 35 per cent. of calcium carbonate) produce nearly white bricks. When the proportion of calcium carbonate is high, gault clays are best mixed with sufficient red clay of another formation so as to reduce the proportion of calcium carbonate in the mixture to not more than 25 per cent.

Some of the white bricks in Suffolk are made by mixing a red-burning clay with a sufficiently large quantity of chalk in a wash-mill, and some of the red surface clays of some parts of Yorkshire are made to yield a whitish brick by mixing them with magnesian lime (from dolomite) in a slaked condition. These clays are naturally wet when dug and the lime is valuable, as it absorbs the moisture in the clay without the necessity of drying it before grinding.

The effect of minute proportions of colouring agents naturally present as impurities in white-burning materials and also the effect of the atmosphere in the kiln, are clearly shown in Table XXIII, due to W. H. Yates and H. Ellam.[1] It may be explained that the *biscuit ware* is the unglazed material ; the *glost ware* is the biscuit ware which has been covered with a transparent, colourless glaze and re-fired at a lower temperature ; the results shown in the last column were obtained by reheating the ware at about 900°–1000° C. among articles which had been decorated with over-glaze colours (p. 96) which required to be fired at this temperature.

When bone china ware is fired under reducing conditions it may assume a bluish shade, which is attributed by Moore and Mellor to the partial dissociation of the bone ash (calcium phosphate) and the resulting formation of ferrous phosphate. A larger proportion of ferrous phosphate is formed, according to J. W. Mellor,[2] when the china ware is deficient in Cornish stone or contains too large a proportion of clay. On the other hand, the higher the proportion of alkali the less is the liability to form ferrous phosphate.

[1] *Trans. Eng. Ceram. Soc.*, **17**, 120 (1917–18).
[2] *Ibid.*, **18**, 497 (1918–19).

TABLE XXIII.—*Effect of Composition and Firing on Colour of Bone China Ware*

Per cent. of Ingredients.			Colour of Biscuit.	Colour of Glost.	Colour after passing through Enamel Kiln.
China Clay.	Bone Ash.	Cornish Stone.			
100	0	0	Cream.	Cream.	Cream.
80	20	0	Brown.	Slightly paler.	Brown increased.
80	0	20	Yellow.	Shade lighter.	Brown.
60	40	0	Pink.	Red brown.	Red.
60	20	20	Light brown.	Dirty brown.	Slight, where glazed thick.
60	0	40	Cream.	Yellow.	Brown.
40	60	0	Green.	Pale green.	Still paler.
40	40	20	Pale green.	Green much increased.	Brown in patches.
40	20	40	Yellow.	Yellow.	Yellow.
40	0	60	Slight brown.	Slight brown.	Slight brown.
20	80	0	Brown.	Shade lighter.	No change.
20	60	20	Colour very slight.	Colour very slight.	Colour very slight.
20	40	40	,, ,,	,, ,,	,, ,,
20	20	60	,, ,,	,, ,,	,, ,,
20	0	80	Tinge of green.	Tinge of green.	Tinge of green.
0	100	0	White.	White.	White.
0	20	80	,,	,,	,,
0	60	40	,,	,,	,,
0	40	60	,,	,,	,,
0	20	80	,,	,,	,,
0	0	100	,,	,,	,,

It is extremely difficult to produce perfectly white goods, as even minute amounts of iron oxide have a strong power of discoloration. The latter may be minimised when it only occurs to a very small extent by (*a*) the use of a reducing fire during part of the period of burning, or (*b*) by adding a suitable coloring agent to neutralise the colour and so produce a pure white ware. Thus, the addition of a minute proportion of cobalt oxide satisfactorily corrects a faint yellow colour in the wares. This is due to the fact that yellow and blue colours are complementary and neutralise each other, producing an almost perfect white, if the total amount of colour is not too large, otherwise a green colour is produced. The action is the same as in the use of "blue" in laundry work. The prepared cobalt oxide may be added either to the

body or to the engobe or glaze placed upon it. The latter is the cheaper, but the former gives the most dependable results, the cobalt being added either in the form of a very fine powder or of a solution of cobalt chloride or sulphate in water. If the solid material is used, it must be ground extremely fine or it will produce minute blue spots instead of making the ware white. Instead of adding the cobalt oxide direct, it may with advantage be previously mixed with finely-powdered flint or, preferably, with china clay, calcined, and the product ground to an impalpable powder. If a solution of a cobalt salt is used, care should be taken that it is not precipitated by any free alkali in the clay prior to the colour and clay being mixed, or it will form blue spots. When the solution of the cobalt has once been thoroughly distributed through the mass, it may, with advantage, be rendered insoluble by the addition of a solution of sodium carbonate.

Yellow goods (apart from those artificially coloured) may owe their colour to :

(*a*) The presence of only a small proportion of iron compounds, as in fireclays.

(*b*) The presence of finely-divided iron oxide simultaneously with free alumina (p. 101).

(*c*) The presence of a considerable proportion of chalk or other form of calcium carbonate (p. 102) in clays burned in contact with coke or other organic matter.

Thus, true marls or malms are yellowish or whitish when fired, on account of the lime present in them, the London malms burning to a rich brimstone colour.

Buff-coloured Articles.—The buff colour of bricks is due usually to the presence of iron compounds in some form, but the cause of the colour in buff-burning clays is far less clearly understood than that of either the red or white-burning clays. The iron content varies from 0·50 per cent. to 4 or 5 per cent., with an average about 1·5. Buff-burning clays do not burn buff because of the exact amount of iron they contain. So far as the iron content is concerned, they might burn either red or white, and other conditions are far more important than the exact proportion of iron present. Sometimes the buff colour may be due to the effect of the iron compounds partly being reduced in the presence of lime compounds or free alumina (p. 101), though this is not the case with fireclays, unless it is correct to assume that their buff colour, when burned, is due to a compound of iron and alumina.

Fireclays are usually buff colour when burned, but it has never been satisfactorily proved that this is due to the presence of iron compounds. The greater part of the iron in fireclays is in the form of pyrites (p. 103), which forms black spots or blotches or patches of a dark-brown colour. Some fireclay articles have a reddish appearance (termed " flashing," p. 106), due to the oxidation of iron compounds derived from the ash of the fuel used in firing. This usually occurs when an excessive supply of air is allowed to pass through the kiln during the cooling period.

The colour of fireclay articles must not be regarded as a criterion of their quality, as a dark-coloured brick, which, from its colour, might be rejected as too impure, may be more durable than a light-coloured one. Many engineers, architects, and builders consider that a fireclay article which has a good uniform buff colour is the best, their idea being that it has been burned at a high temperature without showing any signs of being affected by the heat. This is an entirely erroneous idea, for

underburned firebricks are light coloured, and those which have been intensely heated are usually highly discoloured. In fact, a fireclay article of apparently poor quality, which is covered with blotches and much discoloured, may be better than one of a pleasant, pale-cream colour. In other words, discoloration is usually a sign of a high firing temperature, and when a firebrick has been heated to a temperature sufficient to produce blotches without the article itself being fused or warped, it is usually reasonable to suppose that it will be able to withstand that temperature when in use, whereas pale-coloured goods which have not been heated so strongly may fail in use.

The presence of *minute* dark blotches of "slag" in firebricks are of little consequence and are not detrimental to their quality, unless very abundant. Even then, if they occur chiefly at the surface, and are not abundant in the interior of the article, they will do little damage, though they create a very unpleasant appearance. Some users insist that the area of the dark spots in firebricks shall not exceed 3 per cent. of the cross-section or face of a firebrick.

Clays which do not naturally produce a buff colour when burned may be made to do so by (i) destroying the colour of a red-burning clay by adding a large proportion of chalk or limestone (p. 102); (ii) by adding iron in the form of a silicate-mineral such as granite, schist, talc, etc., to a white-burning clay; (iii) by adding an iron solution to a clay slip and precipitating the iron by the addition of soda solution; and (iv) by adding a stain containing 95 per cent. of alumina plus 5 per cent. of oxide of iron, derived from ferric chloride solution by precipitation, as in (iii). This last gives the best results, but is costly, and to get the best effects the body must be heated to vitrification.

Brown goods are often produced by iron oxide in a clay, the conditions of firing being such that instead of the iron compounds attaining their full red, as in red bricks (p. 109), the colour is either partially developed or it is converted into a brown by overheating. The imperfect development of the red colour may be due to the presence of lime, alumina, and other substances in the clay, or to vitrification having set in before or after the red tint was fully developed.

The brown colour of some fired clays is due to the presence of manganese compounds.

Artificial Colours

Artificial colours are produced by the use of various chemical substances which when heated to a suitable temperature assume the desired colour. The temperature to which the articles are heated must, therefore, be one which suits the colours. Thus, if the ware requires a high temperature for firing and the colour requires a low one, the ware must be burned first, then coloured and refired at a lower temperature. If, however, the colour will stand the temperature required to fire the ware, the latter may be first coloured and then fired. Where it is desired to mix a colour with the material of which an article is made, that colouring agent must necessarily be able to withstand the temperature at which the article is fired.

The finer colours and those produced by expensive chemicals are usually mixed

with an engobe (p. 96) or glaze, and are then applied to the ware; to mix such colours with the whole of the clay of which the articles are made would not only be excessively costly, but would be an unnecessary waste of colour. Several firms supply colours prepared ready for use by potters and others.

Black articles—or the nearest approach to a true black which can be obtained in pottery manufacture—may be produced by:

(*a*) The addition of a mixture of manganese dioxide and iron oxide to the clay or engobe. Where there is sufficient iron oxide in the clay, the addition of a suitable proportion of manganese dioxide is usually sufficient. The precise colour produced depends on the relative proportion and fineness of the two colouring agents. A red-burning clay with the addition of about $1\frac{1}{2}$ per cent. of manganese dioxide will usually produce a beautiful jet black. It is important to use fine precipitated manganese dioxide; that produced from spent material used in the manufacture of chlorine, etc., is much less satisfactory. If the colour is too brown or violet, the proportion of manganese dioxide should be increased or the iron oxide reduced.

(*b*) The addition of a mixture of iron and cobalt oxides.

(*c*) The addition of iron, manganese, cobalt, and chromium oxides to the clay or engobe.

Grey may be produced by the use of smaller proportions of the same materials as are used for blacks (*supra*), but the iron must not be present in very large proportions when light shades of grey are required. Greys may also be produced by means of iridium oxide or platinum chloride or both, but these are so costly that their use is confined to the most expensive pieces of art ware.

Blue colours are produced on white wares by the addition of cobalt oxide to the clay or engobe. The shade of colour is largely dependent upon the alumina present, a highly-aluminous body giving a sky-blue tint, whilst a siliceous mass, or one containing zinc oxide, usually assumes more of an indigo shade. Blues may be modified by varying the proportion of cobalt and also by the addition of other substances, such as alum or frits.[1]

Violet colours are extremely difficult to obtain; the best are usually produced by a mixture of chromium and cobalt oxides. Under suitable conditions, precipitated manganese dioxide produces an excellent violet.

Green colours are generally produced by the addition of chromium or nickel oxides to bodies containing only a very small proportion of iron oxide, as otherwise the colour will not be pure green. Chromium greens are the most easily produced, and may be modified towards blue by the addition of cobalt oxide. Nickel greens are somewhat uncertain, especially at temperatures above 1100° C., when no other ingredient is used, but with cobalt oxide a fairly reliable olive-green is obtained.

At temperatures above 1200° C., iron silicates impart a greenish-yellow colour

[1] A *frit* or *fritt* is a partially fused mixture of two or more substances, some or all of which could not be used separately on account of their solubility in water. In the process of fritting, chemical combination occurs and insoluble substances are produced. The process of fritting is also used to distribute a small proportion of a strong colouring agent in a large proportion of white or colourless material, so as to produce a lighter tint than would otherwise be possible.

to the ware, whilst when such silicates fuse they become quite green and produce the colour of green bottles.

Yellow colours are, where possible, produced almost entirely by iron oxide, the tints varying from yellow through orange to yellowish brown. For high-class pottery, titanium and antimony oxides or lead chromate may be used. For orange-yellow tints, uranium oxides may be employed. For these tints an oxidising atmosphere is essential, as a reducing atmosphere gives a greenish-grey shade.

Red colours, produced at comparatively low temperatures, are usually due to iron oxide. In vitrified wares, iron oxide seldom produces a pleasing red shade. A rose or pink colour may be produced by the addition of a finely powdered frit (p. 116) of bichromate of potash and alumina, whilst a lilac tint may be obtained by the addition of a little cobalt oxide. Pink glazes may be produced by using a mixture of chromium and tin oxides.

Occasionally bricks are made to appear red by dipping them in, or painting them with (just prior to sale), a slip prepared by mixing Venetian red with water into a pulp, which is pressed through a sieve to break up lumps that are formed in mixing, and then adding enough stale ale or beer to make the stain of a proper consistency. To each gallon of this mixture is added one quarter of a pound of calcined iron sulphate, previously beaten up with a portion of the stain to a thin batter. This is the mordant or fixture, without which the stain would finally wash off from the effects of the rain.

A more durable and permanent stain is made with Venetian red that has been ground with linseed oil to form a stiff paste, or, if the stain is to be of a lighter shade, a mixture of Venetian red and French yellow ochre, both ground fine in linseed oil and beaten up with a small portion of a good turpentine japan to a smooth semi-paste, gradually adding in small quantities while stirring, a mixture of one part (by measure) of 90 degrees benzol or good solvent coal-tar naphtha and four parts (by measure) of turpentine, until the proper consistency of stain is secured. The liquid is strained through cheese-cloth and the coarser particles thrown away, as these would remain on the surface and be of no benefit in sealing the pores of the brick. An excess of oil in the stain is apt to produce "shiners," but has the additional advantage of rendering the bricks waterproof. These pastes are paints rather than ceramic colours.

Brown colours are obtained with iron oxide at a temperature higher than that necessary to produce a good red. This treatment is usually accompanied by a variable amount of vitrification. For the lower temperatures a good brown shade may be obtained by the addition of a little manganese dioxide to a ferruginous body. Thus, the addition of 0·5 per cent. of fine manganese dioxide will produce a beautiful chocolate tint.

Browns may also be obtained by (*a*) mixtures of iron and chromium oxides, (*b*) iron chromate, (*c*) manganese and chromium oxides, (*d*) a frit composed of zinc sulphate and chromium oxide.

To secure the desired colour when special colouring agents are employed, it is most important that the right atmosphere should be maintained during the firing of the ware and that the right temperature should be reached, but not exceeded.

Excessively high temperatures may cause volatilisation of the colour. Very often in producing coloured goods, different effects are obtained on account of variations in the state of the atmosphere in the kiln. Thus, articles intended to be buff may be streaked with red, red ones may be changed to chocolate colour or purplish black, whilst blue ones may be considerably deepened. These accidental shades of colour are often of great beauty, but cannot always be produced as and when desired.

The effect of the atmosphere in the kiln upon various colours is shown in Table XXIV, due to Le Chatelier and Chapney.

TABLE XXIV.—*Effect of Heat on Colours*

Compound of Metal in Colour.	Firing Cone.	Temperature, ° C.	Colour produced in Oxidising Atmosphere.	Colour produced in Reducing Atmosphere.
Chromium .	13	1380	Violet, blue, green, gold, orange, or red.	..
Cobalt . .	,,	,,	..	Blue, green, or rose.
Copper . .	,,	,,	Blue, green, gold, or red.	
Iron . .	,,	,,	Gold, red.	Blue, green.
Manganese .	,,	,,	Violet, blue, green, gold, red.	..
Nickel . .	,,	,,	Violet, blue, green, gold, red.	..
Titanium .	,,	,,	..	Violet, blue, green, gold, red.

The volatilisation of some colours also produces a vari-coloured effect (often of great beauty). Volatile chlorides are largely used for the production of this class of ware, lead chloride being commonly employed. By the use of a chlorinated atmosphere, such as is produced by this means, cobalt oxide will give a blue colour, nickel oxide a brown one, copper oxide green at low temperatures, and iron oxide a very unpleasant yellow. The production of colour effects by partial volatilisation is known as "flowing."

Streaks of colour are often useful as a form of decoration. They are sometimes caused by firing a glaze to such an extent that it vitrifies and flows; by this means very beautiful marbled effects may be obtained.

Variegated colour effects may also be obtained by the process known as "flaming" or "flashing" (p. 106).

THE COLOURS OF CERAMIC MATERIALS OTHER THAN CLAY

The colour of ceramic materials other than clay is not often of great importance except as a very rough indication of their quality, though it should be remembered

that the remarks on p. 114 with reference to the relation between the colour and properties of fireclay bricks apply to most other ceramic articles.

Siliceous Materials.—Pure *quartz* is colourless, but natural quartz is often rendered partially opaque by numerous " inclusions " or bubbles, and it is frequently tinted by iron oxide and other impurities which impart to it a pink, yellow, brown, or purple colour ; sometimes it is so dark as to appear almost black.

Quartzites, if quite pure, would be colourless, but they are invariably tinted by traces of iron and other oxides and so vary from white to a dark brown the purer and more refractory qualities being almost colourless. Many quartzites which appear to be opaque or coloured, consist of transparent, colourless grains, the opacity, and to some extent the colour, being a mass-phenomenon.

Ganister varies from grey to dark brown in colour according to the proportion of carbonaceous matter, iron oxide, and clay present. The individual grains are transparent and usually colourless.

Flint varies in colour from grey to almost black, apparently on account of the carbonaceous matter present in a very fine state of division. The exterior of flints is usually buff.

Chert is similar, but much lighter in colour, as also are *chalcedony* and other forms of amorphous silica. Chalcedony is generally white, grey, pale blue, bluish white, or brown in colour.

Kieselguhr varies greatly in colour according to its purity. The best qualities are white and are composed of colourless grains, but inferior deposits are often coloured deep red or brown by ferric oxide. In some deposits of kieselguhr the red colour of the iron oxide is masked in the raw state by carbonaceous matter, which imparts a greyish tint to the material. On calcination, the carbonaceous material burns away and the red colour is restored. The kieselguhr at Naterleuss, in Germany, is coloured green by the presence of a large proportion of carbonaceous matter.

When heated to bright redness in an oxidising atmosphere, quartzite, ganister, and other siliceous materials are usually white, the less pure ones being pale yellow or buff and often contain dark-brown spots of iron compounds.

Carbon.—*Graphite* is greyish black with a metallic lustre. *Coke* has a steel-grey tint. Their colour is not appreciably altered by heat, but in the presence of air they are gradually converted into a colourless gas.

Carborundum varies in colour according to its form. The crystals vary from pale yellow to grey or blue-black, and the amorphous variety, known as *firesand*, is white when pure, but the commercial material is usually green, grey, or nearly black with a bluish sheen. The colour is not affected by heating to redness.

Silundum, which is formed in a similar manner to carborundum but at a temperature of 1300°–1800° C., is greenish or slate-coloured, but becomes steel-grey when heated above 1800° C.

Bauxite, when pure, is white, but as some iron compounds are generally present its colour is sometimes pale grey, yellow, or even brick-red. The much rarer blue bauxite appears to owe its colour to colloidal ferrous sulphide.

When heated to bright redness in an oxidising atmosphere, bauxite varies from nearly white to a reddish or brown tint according to the iron oxide present.

Crystalline magnesite is colourless, white, or yellowish grey. The cryptocrystalline magnesite is white, yellowish, or brown. *Hydromagnesite* is usually white and resembles chalk. *Breunnerite* is generally grey or yellow when freshly cut, but on exposure the iron compounds present are oxidised and impart a brownish colour to the rock.

When heated to bright redness, pure magnesite remains white, but much of the natural mineral is coloured buff or reddish brown by the iron oxide and other impurities present.

When most samples of pure magnesite are heated to 1500° C. or above (*i.e.* when they are dead-burned), they remain white, but in most commercial samples of natural magnesite the effects of the colouring agents are accentuated and the produce is buff, red, reddish brown, chocolate brown, or black, according to the nature and proportion of impurities present. When different samples from the same deposit are compared, their colour is a useful indication of the extent to which the magnesite has been heated, though the change in colour is much less marked with the purer magnesites. Thus, a properly dead-burned and sintered magnesite containing about 4 per cent. of iron oxide is a dark chocolate-brown colour, but if the same rock has not been heated so intensely it is much lighter. The darkest colours are usually due to a partial reduction of the iron oxide or to the presence of manganese compounds. The difference in colour between pure and slightly ferruginous magnesite is clearly shown in magnesite bricks. Those made from the Styrian magnesite, which contains ferric oxide, are reddish to dark brown or black, whilst those made from the much purer Grecian magnesite are cream, buff, or other light colour, and frequently have numerous dark-brown spots.

Dolomite varies in colour from pale cream to yellowish brown according to the amount of iron oxide present. The colour of calcined dolomite and of any bricks, etc., made from it, is usually yellowish brown.

Lime, when almost pure, is perfectly white, but portions of commercial limes are usually coloured slightly by iron oxide or charred carbonaceous matter. Refractory bricks and blocks made of lime should be almost pure white.

Zirconia.—The natural mixture of zirconia and zircon found at Sao Paulo, Brazil, varies from grey to bluish black, according to its purity. It is a curious fact that the ore richest in zirconia is almost jet black, because pure zirconia is a brilliant white. The baddeleyite found in Ceylon varies in colour from white to grey-brown, bluish black, or dark green. Natural zircon is usually tinted yellow by the iron oxide present, and some specimens are grey-green or red. The colour of pure zirconia when calcined is white if the temperature has not exceeded 1500° C., but above this temperature various colours are developed as a result, according to Ruff and Lauschke, of the formation of nitrides, lower oxides, and black zirconium carbide.

When titanium oxide is present in zirconia, a bluish colour is developed at a temperature of about 1500° C.

Discoloration

The term " discoloration " is applied to materials or articles possessing colours of an undesirable character upon their surface or in their interior. Such a defect is due, in the main, to the same causes as the colours previously mentioned. The principal causes of discoloration are :—

(*a*) Insoluble substances.

(*b*) Soluble substances or " scum."

Other discolorations may frequently be traced to :—

(*c*) Substances derived from the fuel and present in the kiln gases.

(*d*) Substances volatilised from articles adjacent to the ones which are discoloured.

Discoloration by insoluble substances includes several colouring agents mentioned in preceding pages which produce an undesirable appearance.

Blackspots are usually due to ferrous or manganese compounds (p. 111), but sometimes white ware fired in carborundum saggers is discoloured by grey, red, or black stains, due, according to H. Spurrier,[1] to the production of volatile ferro-carbonyl compounds.

Blue discolorations in china are often due to ferrous phosphate (derived from bone ash containing carbon), a deficiency of alkalies in the body, or to the action of reducing gases.

Brown discolorations are usually due to ferric compounds (p. 97), including absorbed vapour of ferric chloride and also the discolorations in china due to ferric phosphate. Some pieces of white china become discoloured with brown patches on prolonged exposure to air ; these discolorations are also attributed to ferric phosphate. For information on brown discolorations of firebricks, see p. 114.

Ferrous phosphate is sometimes white, but on exposure to air it becomes blue or green, and finally develops a brownish crust by oxidation. See also *Brown scum*, p. 123.

Green discolorations may be produced by copper and vanadium compounds ; thus, cupriferous pyrites produces greenish slag spots and vanadium molybdate produces irregular green patches.

Green discolorations may be due to the slight deposition of soot on the goods or to the causes of black discolorations operating on a smaller scale.

Pink discolorations on biscuit ware or buff terra-cotta often indicates that the ware has been heated too rapidly below 700° C., so that the combined water has not been driven off properly.

The red discoloration in some hard porcelain, known as *la malade jaune* or *jaune de cuisson*, is due, according to B. Moore and J. W. Mellor,[2] to the presence of ferric oxide and of oxidising conditions in the first stages of burning. Seger found that a red discoloration which occurs on a yellow-burning clay may usually be cured by alternately heating in a very smoky kiln (*i.e.* in a strongly reducing atmosphere) for some time and then in an oxidising atmosphere, at intervals of eight hours, so as to cause the

[1] *J. Amer. Cer. Soc.*, **4**, 923 (1921).

[2] *Trans. Eng. Ceram. Soc.*, **16**, 58 (1917).

sulphur to be evolved as sulphuric acid and to reduce the iron to a ferrous or to a ferro-calcite state.

Yellow discolorations are often due to ferric compounds (p. 97). For means of correcting a yellowish tinge in china and white earthenware, see p. 113.

Scum is a defect known by a variety of names, such as " whitewash," " nitre," " salt," " mould " (all of which are incorrect), and " efflorescence," " wall white," etc., which more accurately describe it.

The causes and cures of scum have been investigated in great detail by a number of people in recent years, and whilst it is by no means easy to find the cause and remedy for it in any particular case without a considerable amount of investigation, it may generally be said that scum is due to salts contained in the clay or other rock, in the water used in the course of manufacture, or to condensation products settling on the goods whilst in the kiln, especially if a continuous kiln is used.

Less frequently, scum is produced on bricks, tiles, etc., a considerable time after they have been taken from the kiln, and the cause will then usually be found to be improper storage on ground saturated with soluble salts, or to the use of mortar of an unsuitable kind.

Briefly expressed, the main sources and cures of scum are as follows :—

1. Soluble salts occurring naturally in the material itself.
2. Soluble salts produced from other ingredients in the material as a result of " weathering."
3. Soluble substances deposited on or formed in the material during the burning, either by condensation products from the kiln gases or by some chemical reaction taking place within the kiln.
4. Soluble salts contained in the mortar used in erecting a building of the bricks, etc.
5. Soluble salts developed by interaction of the mortar and bricks or tiles.
6. Soluble salts in the water used in the manufacture of the goods, or in building.
7. Soluble salts in the ground on which the goods are stacked before or after sale, or in ashes and other materials in contact with the goods.

White scums are the commonest and include " dryer white," " kiln white," and " wall white," all of which are formed by the accumulation of soluble salts on the surface of the goods before, during, and after firing respectively. They are chiefly due to the presence of calcium, magnesium, potassium, sodium, ferrous or aluminium sulphates, and, occasionally, to other salts such as chlorides and nitrates. These salts are of more frequent occurrence in weathered clay than in a clay or rock which has been freshly dug or quarried. Very small percentages of some of these salts—especially soda, potash, and magnesia—are sufficient to cause an objectionable amount of scum, and cases have been known where as little as 0·01 per cent. of sodium sulphate has spoiled the surface of facing bricks.

White scums are more common with surface clays than with those of greater age, as the former, being nearer to the surface, more easily become impregnated with various soluble salts, whereas deposits which occur at a greater depth have usually been subjected to some natural leaching action, whereby the soluble salts have been removed.

"Kiln white" consists chiefly of calcium sulphate with small amounts of magnesium and alkaline sulphates, and occasionally a trace of alum. It is formed by the action of sulphurous acid in the kiln gases on the lime, etc., in the clay.

A *brown scum* on some fired goods may be due to the presence of soluble iron salts formed by the oxidation of pyrites in the clay or rock to ferric sulphate which, being soluble, rises to the surface of the moist material by capillary action during the drying and is converted to ferric oxide during the firing.

A *grey scum* is sometimes formed if calcareous water comes into contact with a clay. Calcium and magnesium sulphates, when present in a clay, also tend to impart a drab appearance.

A *yellowish* scum may be formed by the interaction of sulphuric acid in the kiln gases with the alumina, lime, and silica in the clay at temperatures approaching to that of vitrification. Seger found a yellowish scum to be produced by the presence of soluble potassium vanadate.

According to Kallauner and Hruda,[1] as little as 0·1 per cent. of vanadium oxide causes discoloration and as little as 0·001 per cent. may cause scumming. The discoloration and scumming may be reduced by the addition of barium carbonate, chloride, or nitrate, which form insoluble barium salts. An excess of barium chloride or nitrate must be avoided or it may increase the scum instead of reducing it.

The yellow-green staining sometimes attributed to vanadium may, according to C. W. Hill,[2] be due to ferrous salts.

Colour Measurement

The measurement of the colour of clays and other rocks, and of the products made from them, has not reached a stage where it can be done accurately. Fortunately, it is seldom necessary, and such comparisons as are required may usually be satisfactorily judged by the naked eye if care is taken to avoid unsuitable lighting. Transparent materials may be compared by means of a colourmeter (Chapter XV), but this is not completely satisfactory, and is quite unsuitable for opaque materials.

HARDNESS

A comparison of the hardness of clays and many refractory materials, both in the raw and fired states, is often a matter of great difficulty, because these materials are not strictly homogeneous and different portions of them have different degrees of hardness, so that no single figure can accurately represent the hardness of the material. For instance, the outside "skin" of a brick or tile is usually much harder than its interior; many firebricks are composed of mixtures of burned clay and quartz, which substances differ greatly in hardness and in many articles, the bulk of the material or aggregate has a hardness which is different from that of the bonding material. When the hardness of a heterogeneous substance is considered, the term usually relates to that of the material as a whole and is, therefore, only capable of a relatively rough measurement.

[1] *Sprech.*, **45**, 333–5, 345–9 (1922).

[2] *Bull. Amer. Cer. Soc.*, **1**, 51 (1922).

Hardness is usually measured by observing the resistance of the materials to (*a*) indentation and (*b*) abrasion by various harder substances. There is no direct relation between the resistance of a heterogeneous substance to indentation and to abrasion, as the latter is not really a measure of the hardness of the material as a whole, but of the bond, for no matter how hard the individual grains of aggregate may be, if the bond is soft and easily abraded the whole material will rapidly be worn away. Hence, the hardness of a heterogeneous substance is closely connected with the cohesion of the various particles.

Resistance to indentation may be measured by a scleroscope or by a Brinel ball (p. 135), but for rough-and-ready comparisons a " scratching test " is chiefly used. A series of minerals of different hardness is used, and each of these is drawn across the material to be tested so as to make a scratch if the latter is softer than the former. When the material to be tested is scratched by one member of the series, but scratches the next softer member, it is said to have a hardness between that of the two members. The series of minerals generally used for the purpose is shown in Table XXV, where they are arranged in what is known as " Mohs' scale." A series of convenient substitutes is also shown in the same Table.

TABLE XXV.—*Mohs' Scale* (*substitutes shown in Italics*)

Hardness No.	Material.
1	Foliated talc.
2	Rock salt or gypsum, or *finger nail.*
3	Transparent calc spar or *copper wire.*
4	Fluor spar, *scratches copper wire.*
4–5	*Ductile iron ; window glass.*
5	Transparent apatite.
5–6	*Blade of good pocket-knife.*
6	Orthoclase felspar.
6·5	*File.*
7	Transparent quartz.
7–8	*Will scratch a knife.*
8	Transparent topaz.
9	Sapphire or corundum.
10	Diamond.

When a substance has a crystalline structure its hardness will vary along different planes and is usually lower in the direction of cleavage than perpendicular to it.

The resistance of ceramic materials to abrasion is usually more important, especially as many of them are subjected to a considerable amount of abrasion when in use. Thus, domestic pottery requires to resist the scratching and rubbing action of

knives, forks, etc.; paving bricks, floor tiles, etc., require to be resistant to traffic; and many refractory materials are required to resist the abrasive and corrosive dust contained in the hot gases in furnaces, kilns, etc., which rapidly wear away any soft portions of refractory material.

The bricks which form the lining of vertical shaft furnaces, such as blast furnaces, cupolas, lime, magnesia, and other calcining kilns, etc., are subject to great abrasion by the descending charges, and it is essential that such bricks should have the necessary resistance to this action and to the differential movements which often occur in shaft kilns, and also exercise a considerable abrasion action.

The manner in which gas retorts and some other appliances made of ceramic materials are charged and discharged also calls for the use of a material which is highly resistant to abrasion both in the hot and cold states. "Rough usage" also has a great abrasive effect, as well as necessitating the use of a material which is resistant to blows and shocks.

The resistance of a ceramic material to abrasion depends upon one or more of the following:—

(*a*) The nature of the material, and especially its texture and hardness.
(*b*) The mode of its preparation.
(*c*) The nature of the bond (if any).
(*d*) The amount of bond (if any).
(*e*) The extent of vitrification.
(*f*) The temperature of the material when it is examined.

Hardness of Raw Materials

The hardness of raw **clays** varies greatly, from less than 1 to more than 7 on Mohs' scale (p. 124); some surface clays are quite soft and can be cut with a knife; others, such as shales and rock clays, are hard, because of the metamorphic changes they have undergone and the pressure to which they have been subjected. Most of the hard clays have at one time been at a great depth below the surface. The clays of most industrial importance are comparatively soft, especially when in a plastic state; some of the harder ones, after being ground to powder and wetted, become quite soft and plastic. Clays such as loams, containing much sand, are, when dry, harder than purer clays. Marls and fireclays vary greatly in hardness, according to their mode of formation and location. Most of them, when in the dry state, can be easily cut with a knife, but some are hard enough to scratch glass. This scratching is largely confined to siliceous (quartzose) impurities in the clay and not to the clay itself.

As clays are usually converted into a plastic paste, or into a slip or cream before use, their hardness is only of importance in so far as it affects the methods to be employed in grinding them to powder or otherwise preparing them for use. Clays which cannot readily be crushed to the required fineness are naturally easier and cheaper to prepare and are, therefore, more desirable than very hard materials which require much power to reduce them. The hardness of a raw clay has little or no effect on that of the finished products.

A property similar to the Brinell hardness of raw clay is the " pressure of fluidity," as A. S. E. Ackermann[1] found that if a horizontal disc of metal is placed on plastic clay and loaded, each increment of load causes an increase in the penetration up to a certain critical point, at which the disc continues to sink at about ten times the previous rate without any increase of the load. This critical point is termed the pressure of fluidity and varies according to the amount of water in the clay and, therefore, to the plasticity; it is discussed in Chapter VI in connection with the mobility of clay pastes.

Silica has a hardness of 7 on Mohs' scale, but many siliceous materials in which individual grains are very hard may be easily crushed, as the bond which unites these particles is quite weak. For the same reason, the individual grains of silica in articles made of that material are much harder than the average of the articles, on account of the softness of the bond.

Aluminous materials vary greatly in hardness; bauxite usually has a hardness of 1–3 on Mohs' scale, whilst corundum or alundum has a hardness of 9–10 and is one of the hardest substances known.

Magnesite varies in hardness according to the form in which it occurs. Coarse crystalline magnesite usually has a hardness of about 4 on Mohs' scale, whilst cryptocrystalline magnesite has a hardness of 3–5 and hydromagnesite a hardness of 3–4.

Carbides and carboxides are extremely hard, corresponding to 9–10 on Mohs' scale, being harder than crystalline alumina (9), but not so hard as diamond (10). The hardness of various minerals which are used in the ceramic industries is shown in Table XXVI.

TABLE XXVI.—*Hardness of Ceramic Materials on Mohs' Scale*

Material.	Hardness.	Material.	Hardness.
Baddeleyite	6·5	Kaolinite	1–2·5
Bauxite	1–3	Magnesite	3–5
Brookite	5·5–6	Magnetite	5·5–6·5
Calcite	3	Monazite	5–5·5
Chromite	5·5	Quartz	7
Common clay (dry)	0–7	Rutile	6–6·5
Corundum	9	Sand	7
Cyanite	7·25	Sillimanite	6–7
Dolomite	3·5–4	Spinel	8
Graphite	1–2	Tantalite	6
Hæmatite	5·5–6·5	Titanite	5–5·5
Hydromagnesite	3·5	Tridymite	7
Ilmenite	5–6	Zircon	7·5

[1] *Trans. Society of Engineers*, 1910.

Hardness of Burned Ceramic Materials

Burned clay is much harder than raw clay and articles composed of it, either alone or mixed with other materials, may conveniently be arranged [1] in two groups, according to their hardness :—

Group I.—Soft wares, which can be scratched by iron, including fired sandy-clayey bodies, such as bricks, cooking utensils, crucibles, jars, unglazed earthenware, faience, roofing tiles, and most refractory materials.

Group II.—Hard wares, which cannot easily be scratched by steel, including fine earthenware, ceramic stoneware, pipeclay ware, flint ware, and hard china.

Building Bricks.—The hardness of building bricks is seldom of much importance, as, in the ordinary way, they are not required to be highly resistant to abrasion. Most well-burned bricks are rather harder than sandstone. Very soft bricks should not be used, except, possibly, as panels in interior work, as they are generally underburned and deficient in strength and resistance to the weather.

Bricks are not of strictly uniform hardness throughout their mass and though for many ordinary purposes they may be regarded as uniform, the surface is usually harder than the interior on account of the greater pressure applied to it. Machine-made bricks vary quite appreciably, as is shown in Table XXVII, due to H. Le Chatelier and B. Bogitch.[2]

Table XXVII.—*Hardness of Building Bricks* (*Brinell*)

	Portion of Brick Tested.	
	Upper or Piston Side.	Lower or Lifter Side.
Brick No. 1 . . .	5·4	5·6
,, No. 2 . . .	5·6	5·6
,, No. 3 . . .	5·9	6·3

These variations are due to the manner in which the bricks are manufactured and largely unavoidable.

The Brinell hardness (p. 135) of various bricks, compared with metals, is shown in Table XXVIII, due to H. Le Chatelier and B. Bogitch.[2]

[1] Brongniart, *Treatise on the Ceramic Arts.*

[2] *La Ceramique*, **371**, 17–18 (1919).

TABLE XXVIII.—*Brinell Hardness of Various Materials*

Material.	Diameter of Depression.
Copper	4·5
Lead	10·1
Hard face brick	4·5– 8·8
Soft face brick	6·8–12·0
Fireclay brick	6·0– 6·2
Hard silica brick	5·0– 5·1
Tender silica brick	10·1–10·7

The resistance of some building bricks to abrasion as measured by the sandblast method (p. 134), is shown in Table XXIX, due to E. Orton.[1]

TABLE XXIX.—*Hardness of Building Bricks* (*Sandblast*)

Material used for Bricks.	Average Loss under Sandblast.
	Grams.
⅔ shale, ⅓ plastic clay	189
Shale	81
Surface clay	110
Sandy shale and surface clay	235
Shale	113

Vitrified or clinker bricks are, when cold, much harder than ordinary building bricks, as the vitrified or fused material in them produces a very hard bond. According to the American standard, as adopted by the National Brick Manufacturers' Association and the American Society for Municipal Improvements, clinker bricks should have a hardness, according to Mohs' scale, of not less than 6·5 on an average (*i.e.* between that of felspar and quartz), and no individual sample should have a hardness less than 6·0.

Vitrified bricks, when used for roads, etc., require to be specially resistant to abrasion, and, according to the specification of the American Society for Municipal Improvements, such bricks should not lose more than 14 per cent. of their weight

[1] *Trans. Amer. Cer. Soc.*, **14**, 180 (1912).

when subjected to the Standard Rattler Test, and no one brick should lose more than 18 per cent. of its weight. The " Rattler Test " is described in Chapter IV.

E. Orton [1] gives the following results of the resistance of paving bricks to abrasion, the test being that described on p. 134.

TABLE XXX.—*Hardness of Paving Bricks* (*Sandblast*)

Material used for Brick.	Average Loss under Sandblast.
	Grams.
Shale	74
,,	72
,,	69
,,	74
Alluvial clay	87 (laminated)
Shale	65
,,	98
,,	89 (brittle)
Fireclay	89
Fireclay and shale	69
,, ,,	72
Shale	101
,,	101
,,	122
Shale and fireclay	101
Shale	92
,,	84
,,	72

Roofing tiles should be sufficiently hard to be handled without chipping and to prevent them from being damaged by frost. They should not be vitreous or they will " sweat " when in use. A good roofing tile should usually be difficult to scratch with a piece of steel ; roofing tiles which are harder than steel are generally too hard and vitreous. The desired hardness is largely determined by the manner in which the tiles are fired in the kiln. The temperature usually needed to secure roofing tiles of satisfactory hardness is between Cones 04 and 1*a*.

Floor tiles should be sufficiently hard to resist any abrasion to which they may be subjected. F. B. O'Connor tested the resistance of various floor tiles by the method described on p. 134 with the following results :—

[1] *Trans. Amer. Cer. Soc.*, **14**, 180 (1912).

TABLE XXXI.—*Resistance of Floor Tiles to Abrasion*

Type of Tile.	Loss in Thickness, per cent.		
	Pressure Applied, lbs. per sq. in.		
	4·25	4	3·75
Buff tiles . .	12·21	14·32	3·78
Red ,, . .	21·24	10·16	12·00
Buff ,, . .	21·57	21·14	..
Red ,, . .	35·55	6·89	..
Buff ,, . .	29·80	..	..
Red ,, . .	18·43	..	..

Fireclay bricks vary greatly in hardness, some being sufficiently soft to crumble when cut with a steel blade, whilst others are harder than steel. The hardness depends to a large extent upon the temperature at which the bricks are fired; the higher the finishing temperature the harder will be the bricks, and soft bricks are usually underburned.

The hardness of fireclay bricks by the Brinell method is shown in the Table on p. 128. The resistance to abrasion of various bricks, tested by M. L. Hartmann and J. E. Kobler, is shown in Table XXXII, the method of testing being that described on p. 134.

TABLE XXXII.—*Resistance of Refractory Bricks to Abrasion*

Kind of Brick.	Depth of Cut when Cold.
	Inch.
Carborundum brick . .	0·1–0·2
Zirconia brick . . .	
Bauxite brick . . .	
Grade C fireclay . . .	0·05–0·07
Magnesia brick . . .	
Chrome brick . . .	
Silica brick. . . .	0·17
Grade A fireclay . . .	0·25–0·26
Grade B fireclay . . .	

Nesbitt and Bell, who used a similar method for determining the resistance to

abrasion, found that hand-made fireclay bricks were less resistant than machine-made ones, hand-made bricks being cut by abrasion to a depth of 0·04 inch in five minutes, whilst machine-made bricks, made by subjecting clay containing 7 per cent. of moisture to a pressure of 1500 lbs. per sq. inch, were cut to a depth of only 0·02 inch.

Fireclay bricks when heated to a temperature below the melting-point are more resistant to abrasion than when they are cold, but when at or above the sintering temperature the presence of molten material in them reduces their hardness and renders them much less resistant to pressure and abrasion. Sometimes, when bricks are taken out of a kiln, they appear to have softened greatly and become seriously distorted; this is not always the result of exposure to a high temperature, but is sometimes caused by condensed steam softening the freshly-set bricks some hours before their temperature has been raised appreciably above that of the atmosphere.

Renegade and Desvignes[1] have found that there is no relation between the hardness of fireclay bricks at high temperatures and their fusion point expressed in cones. They also found that alumina does not appreciably affect the hardness at high temperatures, but the presence of more than 1 per cent. of alkali has a marked detrimental effect.

The resistance to abrasion of various refractory materials at a temperature of 1350° C. is shown in Table XXXIII, due to M. L. Hartmann and O. A. Hongen,[2] the tests being carried out as described on p. 134.

TABLE XXXIII.—*Resistance of Refractory Materials to Abrasion at* 1350° *C.*

Material.	Depth of Cut in Inches.
Bonded carborundum (carbofrax A)	0·01
,, ,, (carbofrax B)	0·30
,, ,, (carbofrax C)	0·01
Grade A fireclay	0·11
Recryst. carborundum (refrax) .	0·07
Bauxite	0·04
Zirconia (natural)	0·06
Grade B fireclay	0·09
Grade C fireclay	0·07
Chrome	0·27
Silica	..
Magnesia	2·50

[1] *Chaleur et Industrie*, **3**, 965 (1922).
[2] *Brick and Clay Record*, **56**, 934 (1920).

Silica bricks are composed of hard grains, but the bond is soft, so that the bricks are readily rubbed down, and they only resist abrasion to a very small extent. The hardness of the individual grains is equal to that of quartz (p. 126). The greater the proportion of lime used in making the bricks the harder will they be, as their resistance to abrasion is entirely dependent on the bond formed by the combination of lime and silica, and unless a sufficient amount of this bond is produced the particles of quartz, etc., are only feebly held together.

Silica bricks which have not been burned at a sufficiently high temperature are very soft and easily abraded. Well-burned bricks are harder and emit a good " ring " when struck.

W. Emery and L. Bradshaw [1] found that hand-made silica bricks were less resistant to abrasion by sandblast than machine-made bricks. The average loss of weight by this treatment of six bricks of each kind was as follows :—

Machine-made bricks . .	106 grams.
Hand-made bricks . .	143 grams.

This corresponds to a difference of 26 per cent. in the respective resistances to abrasion.

The hardness of silica bricks by the Brinell method is shown in Table XXVIII and by Hartmann and Kobler's method in Table XXXII.

Fused silica is not so hard as some forms of glass, though harder than others. Its hardness, as determined by Hertz and Auerbach, is shown in Table XXXIV.

TABLE XXXIV.—*Hardness of Fused Silica and Glass*

Material.	Absolute Hardness.	Mohs' Scale.
	Kg. per sq. mm.	
Quartz glass . .	223	5
Common glass . .	130–265	4–6

Magnesia bricks are fairly resistant to abrasion at atmospheric temperatures, but they are very soft at high temperatures. The resistance of magnesia bricks in the cold and at 1350° C. is shown in Tables XXXII and XXXIII.

Fused magnesia has a hardness of 5–6 according to Mohs' scale.

Bauxite bricks vary in hardness according to the material of which they are made. Their hardness is increased if the bauxite contains a moderate percentage of iron oxide, as, when heated to high temperatures, such bauxites produce a material corresponding to emery, and of such intense hardness that it can scarcely be cut by steel tools. At high temperatures they appear to be very resistant to abrasion (see Table XXXIII).

[1] *Trans. Eng. Cer. Soc.*, **19**, 73 (1919–20).

Carborundum bricks are extremely hard, and an angular fragment from them will readily cut glass. The resistance of carborundum bricks to abrasion in the cold is shown in Table XXXII. At high temperatures some carborundum bricks appear to be extremely resistant to abrasion, more so than any other form of refractory brick. This is well shown in Table XXXIII.

Zirconia bricks vary in hardness according to the bond used. Zirconia itself is soft and remains so, according to H. C. Mayer, even when it has been heated to above 1427° C. The same authority has stated that a brick made of wet-ground material, containing 84 per cent. of zirconia, was flint hard ; the nature of the bond was not stated. According to R. C. Gosrow, zirconia bonded with magnesian chloride and fired at 1600° C. is extremely hard and scratches glass. This mixture retains its hardness when heated to a still higher temperature, zirconium carbide being sometimes formed.

Chrome bricks are fairly resistant to abrasion in the cold, but at high temperatures they are rather soft (see Table XXXIII).

Glazed ware should be sufficiently hard to resist the abrasion to which it is subjected in ordinary use. Domestic earthenware is scarcely hard enough for severe use, as it is too easily scratched by knives and forks. Bone china is much better in this respect, and the " hard porcelain " of the Continent is the hardest and most resistant of all such ware.

A useful method for comparing the hardness of glazed ware is that used by G. Blumenthal, jun.,[1] and described on p. 136. The following figures show the hardness of various glazes tested by him :—

TABLE XXXV.—*Hardness of Glazes*

Whiteware Glazes.			Porcelain Glazes.	
No.	Cone 4.	Cone 6.	No.	Cone 16.
W 1	246	249	P 1	356
W 2	226	..	P 2	370
W 3	224	284	P 3	346
W 4	214	280	P 4	334
W 5	220	261	P 5	321
W 6	218	276	P 6	306
W 7	253	300	P 7	336
W 8	258	284	P 8	342
W 9	213	280	P 9	354
W10	224	296	P10	349
W11	240	286		
Mean	230	279	Mean	348

[1] *J. Amer. Cer. Soc.*, **4**, 896 (1921).

Determination of Hardness

Methods of determining hardness may be divided into two groups : (*a*) those in which the hardness is measured by the amount of material removed from a sample by abrading or grinding it with some other substance—the so-called " abrasive tests," and (*b*) those in which the material to be tested is scratched or indented by another material, *e.g.* by pressure from a ball, cone, or edge-tool, to an extent depending on their relative hardness.

Abrasive tests are of two kinds : (*a*) those in which the sample is pressed against the abrasive material, and (*b*) those in which the abrasive is projected on to the sample to be tested.

Bauschinger's abrasion-testing machine consists of a horizontal cast-iron plate or disc, 2 feet 6 inches diameter, revolving at 30 revs. per minute. The sample, for instance half a brick, is weighed and is then pressed on to the disc with a pressure of 75 lbs. The disc is charged with 20 grams of emery powder and revolved 22 times. The disc is then recharged with the same weight of emery and again rotated the same number of times, the process being repeated until the disc has been rotated 110 times. The loss in weight sustained by the sample is then measured and, if desired, further tests after 220, 330, or 440 revolutions may be made. The abrasion is measured by $\frac{S}{A}$, where S is the loss in weight and A the area exposed to abrasion, or the loss in weight may be divided by the volume or weight of the sample.

F. B. O'Connor [1] has tested the resistance of floor tiles to abrasion by placing them in contact with a revolving table, 4 feet diameter, revolving at 1500 revs. per hour, the table being supplied at a uniform rate with 2 litres of dry crushed quartz of 20–30-mesh. The tests were continued for 1 hour, several different pressures being applied, and after the conclusion of each test the thickness of the tile was measured in eight places and the mean taken. The results obtained are given on p. 130.

M. L. Hartmann and J. E. Kobler [2] have tested the resistance to abrasion by cutting a groove in the ends of each brick to be tested so as to expose the maximum area to cutting and then applying the bricks at a constant pressure of 25 lbs. for 5 minutes to a carborundum grinding wheel of grit 16 and grade 1, 12 inches diameter and with a 2-inch face, running at a constant speed (512 revs. per minute or 1560 feet per minute). The depths of the groove before and after the test were measured ; the difference represents in linear inches the abrasion during a 5 minutes' test. Results obtained by this test are shown in Tables XXXII and XXXIII.

C. E. Nesbitt and M. L. Bell [3] used a carborundum wheel, of grit 16 and grade 16, 18 inches diameter and 2 inches thick, revolving at 1640 feet per minute. The sample was pressed against the wheel under a pressure of 100 lbs. per square inch for 5 minutes and the depth of cut measured.

The *sandblast test* is typical of the methods in which the abrasive is projected on

[1] *Trans. Amer. Cer. Soc.*, **15**, 233 (1913).
[2] *Amer. Electrochem. Soc.*, **37**, 717–20 (1920).
[3] *Metall. and Chem. Eng.*, **15**, 205–212 (1910).

to the material to be tested. Various modifications of the test have been devised; that suggested by the U.S. Bureau of Standards is very convenient. The sample is weighed and then mounted with its face in a vertical position and immediately behind an iron plate in which is an aperture 6 cm. diameter, so that the area exposed to the action of the sand is 28·27 square cm. Standard Ottawa sand of 20–30-mesh is then projected on to the sample through a nozzle $\frac{1}{2}$ inch diameter at a pressure of 20 lbs. per square inch for 3 minutes, the distance between the exposed face of the sample and the nozzle being 12 inches. The effect of the sandblast is measured by the loss in weight during the test.

Emery and Bradshaw used a similar method with Standard Leighton Buzzard sand of 20–30-mesh projected from a nozzle 0·275 inch diameter at a pressure of 7 lbs. per square inch for a period of 4 minutes, the surface to be tested being 7 inches from the nozzle.

Indentation or scratching tests are much older than abrasion tests, one of the earliest scales of hardness being that devised by Mohs, which is still in general use. It is based on the ability of a mineral to scratch one mineral in the series and to be scratched by the next harder mineral in the series. Mohs examined a large number of substances and selected ten, which he numbered according to their hardness, as shown in Table XXV, in which a number of other convenient substances of equal hardness are also shown.

The chief objection to Mohs' scale is that the minerals used as standards themselves vary in hardness to an appreciable extent, but it is very useful for preliminary tests. A series of substances of similar hardness may also be placed in the wrong order if variable pressure is applied when testing them. To overcome this difficulty, Turner [1] makes the scratches with a diamond attached to one end of a balanced lever capable of moving vertically on a knife-edge and of being rotated. The lever is provided with a sliding weight and is graduated, so that each division of the scale corresponds to a weight of 10, 20, 30, or 40 grams at the diamond point. The sample to be tested is polished and is then tested by drawing it under the diamond point, whilst the latter is under various pressures, until a decided scratch is produced. The weight (in grams) on the point when this is effected is taken as a measure of the hardness. Martens modified this test by specifying that the scratch produced must be 0·01 mm. wide. This method was at one time used for measuring the hardness of metals, but it has not been extensively employed for ceramic materials.

More accurate comparisons of hardness can be obtained by measuring the size of the indentation produced, but for this purpose a " scratch " is not so convenient as a circular indentation. Consequently, accurate comparisons of hardness are now chiefly made by means of the *Brinell ball test*, in which, as modified by Le Chatelier and B. Bogitch [2] to make it applicable to ceramic materials, a piece of thin lead foil, 0·05 mm. thick, previously blackened by the action of sulphuretted hydrogen in slightly acid solution and then dried and smeared with vaseline which is largely removed again, so as to leave a matte surface, is laid on the surface to be tested, and

[1] *Proc. Birm. Phil. Soc.*, **5**, Part II. (1886).
[2] *La Ceramique*, **371**, 17–18 (1919).

on this is placed a hardened steel ball, 17·5 mm. diameter. A pressure of 500 kg. is applied to the ball for exactly 60 seconds, after which the depth or the diameter of the indentation is measured. The hardness is then calculated from the formula :

$$H=\frac{P}{1{\cdot}5708\ D(D-\sqrt{D^2-d^2})},$$

where H is the hardness, P the load in kg., D the diameter of the sphere, and d the diameter of the indentation. It may also be calculated from the formula :

$$H=\frac{P}{3{\cdot}1416\ De'},$$

where e is the depth of the indentation and is equal to $\frac{1}{2}(D-\sqrt{D^2-d^2})$.

For hard materials, a pressure of 3000 kg. is usually required, but for softer ones 500 kg. is sufficient. The results obtained by the use of different weights are not strictly comparable, so that, as far as possible, a constant weight should be employed.

When testing metals, no foil is used, but it is essential with most ceramic materials, as otherwise the indentation is not clearly defined.

E. Renegade and E. Desvignes [1] measure the hardness of refractory materials at high temperatures by supporting a cylindrical test-piece on a graphite block in an electric furnace of the Rosenhain type and pressing upon it a 90° cone by means of an amplifying lever applied through a rod of Acheson graphite, the depth of penetration being measured by a rule shaped at the end to fit the hollow formed by the cone.

A modification of the Brinell test was used for testing the hardness of glazes by G. Blumenthal, jun.,[2] who allowed a hardened, rounded tungsten-steel point to bear on the glaze surface for 3 minutes under a pressure of 50 lbs. and then measured the diameter of the indentation. The hardness was calculated from the formula :

$$H=\frac{P}{\pi tD},$$

where P is the load, D the diameter of the rounded point, and t the depth of the indentation is

$$\frac{D}{2}-\sqrt{\frac{D^2}{4}-\frac{d^2}{4}},$$

where d is the diameter of the indentation.

In the *Shore scleroscope*, a hardened steel cylindrical hammer about $\frac{1}{4}$ inch diameter and $\frac{3}{4}$ inch long, with a striking top about 0·02 inch diameter and weighing about $\frac{1}{12}$ oz., is allowed to fall through a glass tube from a height of 10 inches on to the material to be tested. The height of the rebound is measured on a scale and the hardness calculated from the figure so obtained. Although the scleroscope is regarded as measuring the hardness of a material it does not really do so, but only the elasticity ;

[1] *Chaleur et Industrie*, **3**, 965 (1922).
[2] *J. Amer. Cer. Soc.*, **4**, 896 (1921).

it does not give very concordant results with ceramic materials and is not used to any great extent, the modified Brinell test being more suitable.

MINOR PROPERTIES

Ring.—The clear ringing note or " ring " which some burned ceramic materials emit when struck is often a good indication of the extent of the burning and the absence of cracks. A dull " ring " is usually due to the presence of small cracks, some of which may cause serious trouble if used under exacting conditions, whilst others are so minute as to be of little or no importance. The note emitted by silica bricks made from pre-calcined quartz is much duller than that from bricks made from the raw material; the difference is probably due to extremely minute cracks in the individual grains.

Whilst of considerable use as a rough test, too much reliance must not be placed upon the sound emitted when a sample is struck, because the note depends on so many factors, some of which may affect the " ring " without being necessarily harmful.

Feel.—Most ceramic materials and many others have a characteristic " feel," which may be (*a*) smooth, (*b*) rough, (*c*) meagre or harsh, (*d*) greasy, soapy, silky, or unctuous.

Most refractory materials belong to the first three groups, whilst many clays are included in the last one. Some materials may be classed in two groups simultaneously; thus, china clay and dry ball clay are smooth and unctuous; many fireclays feel " rough," but a freshly-cut surface, when rubbed with the fingers, has a slightly greasy feel. As the tongue is often more sensitive than the fingers, it has long been the custom to compare some fine clays by placing a small portion in the mouth and " working " it with the tongue. By this means the presence of a very small proportion of grit in an otherwise impalpable material is readily recognised.

Experts can readily distinguish different varieties of porcelain and other ware by the " feel," and this property is often very useful as a supplementary indication of the nature of a material.

Odour.—Many clays, when moist, have a characteristic earthy odour, which probably is due to carbonaceous matter present, as it can be removed by treatment with a solution of iron saccharate, the odour being transferred to the latter. When heated to redness, the characteristic odour is lost. Impurities may sometimes be detected by the odour they emit, especially when heated. Thus, some clays and alum shales have a sulphurous odour on account of the pyrites present in them. This is particularly noticeable when the clay is freshly cut or heated to redness in a closed vessel.

Sectility and Fissility are two closely related terms, indicating that a material to which they are applied can readily be cut, in at least one direction. Shales are of this character, though the " cutting " is possibly more in the nature of " splitting," or separating the existing laminæ of which the material is composed. In order to be sectile a material must usually be moderately soft, but a hard material composed of thin sheets united by a soft cement will be fissile in a direction parallel to the sheet.

The most sectile clays are ball and china clays when almost dry, and also some of the surface clays. Harder or leaner clays are friable rather than sectile, so that when a knife is applied to them they are crushed rather than cut.

Most ceramic materials lose their sectility when heated to redness, but this property is retained to a large extent by certain rather soft bricks (known as *cutters*), and by many tiles. This property is due to the large proportion of sand present and to the heat-treatment and temperature attained in the kiln being insufficient to produce a very strong bond. It is important with such articles, as it enables the brick- or tile-layer to cut them to different sizes in order to fit them into special places. It may be noted that silica bricks are more difficult to cut than those made of fireclay, chiefly on account of their coarser texture and greater brittleness.

Friability may be regarded as the converse of resistance to abrasion; it is considered more fully in Chapter IV.

CHAPTER IV

STRENGTH AND ALLIED PROPERTIES

THE term *strength* is a very vague one and is used in several ways. The most frequent use of the term " strength " in connection with ceramic materials is to indicate the ability of an object or mass to retain its shape when various mechanical forces are applied to it under different conditions. In this sense, the strength of a material is due to the cohesion of the particles of which it is composed and the resistance to pressure of the individual grains, especially those forming the coarser aggregate.

If a material fails suddenly when subjected to a sharp blow or other sudden shock, it is said to be *brittle* ; if it is gradually crushed it is *friable*, but if it gradually yields under a succession of blows and forms a coherent mass of different shape, it is termed *malleable*. If its shape can be altered by pulling one portion of it or by passing it through a small aperture it is said to be *ductile* or *plastic*, and if it shows great resistance to such treatment or to bending it is regarded as *tough*.

A material which regains its original shape as soon as the applied force is removed is termed *elastic*, and if a hard object after falling on it is caused to rebound to a considerable height the material is said to be *resilient*.

When the shape of a mass can be altered by bending it is said to be *flexible*. Whenever a force applied to a material causes alteration in its shape the material is said to be *deformable*, and the relation of the change in shape to the force applied is known as the deformability of the material.

The term *durability* introduces a time element, and it is measured by the length of time the required property, such as strength or toughness, is maintained. Thus, material may have a high resistance to crushing when new, but the conditions under which it is used may be such as to reduce its strength in this respect within a short period. Such a material or article could not be regarded as " durable " under the prevalent conditions.

All these properties are closely related in various ways to the " strength " of ceramic and other materials. As the strength of any material is due to a complicated series of qualities, different means are employed to express different kinds of strength, and no single figure can possibly represent the strength of an article in every respect. Thus, two materials may simultaneously have a high crushing strength and a great resistance to a tensile or " pulling " force, yet they may behave quite differently with respect to their malleability or ductility, etc. Consequently, each aspect of

the strength of a material must be considered separately, after which the combination of several of these properties may be considered.

Cohesion is the force which holds the particles of a mass together; it may be regarded as the force of attraction between the atoms or molecules of a material, and, according to its intensity, a mass may be rigid like a brick, fluid like water, or it may possess various intermediate characteristics such as malleability, plasticity, etc. It is closely related to "Binding Power" (p. 141).

Cohesion is measured by the force required to separate the particles from each other, and, according to the purpose for which the material or article is to be used, its cohesion is judged from its crushing strength, ductility, etc. As the simplest conception of cohesion is the force holding the particles together, it is measured most conveniently as the converse of the force needed to tear them apart, *i.e.* the *tensile strength.* This is difficult to determine accurately in the case of a soft, plastic paste, but quite easy with a stiffer paste or a fairly rigid solid, such as a piece of dried or burned clay, and a knowledge of it is often of great value in investigating the properties of ceramic materials at different stages of manufacture or when they are in use. A high tensile strength in a plastic material is very desirable as it facilitates the manufacture. In dried materials, a high tensile strength lessens the risk of damage in handling and in such irregularities of treatment as heating the material too rapidly during the drying or burning. In the production of vitreous ware, such as porcelain, where there is a considerable proportion of fluid present towards the end of the burning process, a high tensile strength at a high temperature is essential, as, otherwise, the distortion of the mass would be so great that many desirable shapes could not be produced.

A high tensile strength is also important in the case of some finished articles, such as the large crucibles used for melting steel; these are lifted out of the furnace with their contents, a pair of tongs being used, and are carried several yards before being emptied. The weight of their contents exerts a great tensile stress, especially as the materials of which the crucibles are made is somewhat soft at the temperature of molten steel. The walls of the "pots" used for melting glass must also have a high tensile strength in order to withstand the conditions under which they are used. Equally important is the tensile strength of the glazes applied to ceramic materials. The thin film of glaze is subject to complex forces connected with its surface tension and allied phenomena, and unless the glaze is able to accommodate itself to these various stresses it will eventually crack or "peel." Glaze with a high tensile strength will stretch considerably before it will crack, and so will provide a permanent protection under conditions where it would be unattainable with a weaker glaze. This characteristic was formerly thought to be best obtained by using glazes with a high degree of elasticity—an idea which seems to be incompatible with such materials, but R. Rieke has shown that in this connection a high tensile strength is of greater importance than elasticity.

The determination of the tensile strength of ceramic materials has been greatly neglected and few published results are available. It is now being increasingly recognised that comparisons of tensile strength are often just as important as, and

sometimes more so than, those of some other properties. A description of the methods of determining the tensile strength will be found near the end of the present chapter.

Binding power is closely related to cohesion and to tensile strength, but differs from them in at least one important respect. The " binding power " is that which enables a material to act as a cement or binding agent in uniting particles of other materials to which it is applied or with which it is mixed. The term is used in a special sense in connection with certain ceramic materials, as being that power which enables a plastic clay to be mixed with a considerable quantity of non-plastic material, and to produce a mixture which possesses plastic properties and ample tensile strength for the purposes for which it is required. The binding power of clay is usually estimated by mixing the clay with various proportions of sand or other non-plastic material and determining the tensile compression and transverse strength of the mixture either in the plastic or dry state. The choice of a non-plastic material must depend on the purpose of the investigation ; a right selection is very important, as a material may show a higher strength with one kind of sand than with another, or different results with the same sand ground or screened to different degrees of fineness.

The binding power is an extremely important property of plastic clays, as it affords a simple and excellent means of reducing their shrinkage on drying and heating to within convenient limits and enables many mixtures having very desirable properties to be prepared with a facility which would otherwise be impossible. Binding power is often confused with " plasticity," though the two properties are quite distinct, and some plastic materials are seriously deficient in binding power. The chief connection between the two is that when a material possessing binding power is mixed with a non-binding material the mixture may be plastic. Thus, a mixture of linseed oil and whiting in suitable proportions produces a plastic mass (putty), but neither the oil nor the whiting are individually plastic. The oil has, however, a considerable binding power. Unless the proportion of oil is excessive, the plastic mass of putty will differ from a clay of equal plasticity in being almost devoid of binding power (see also Chapter VI).

The determination of binding power is described in Chapter VI.

Brittleness is the property possessed by some materials which causes them to break or " split " when allowed to fall on a hard floor or when they are subjected to a sudden, single blow. It is due to a lack of sufficient cohesion of the particles and to some extent to the hardness of the material, which prevents it from yielding under sudden stress and so causes it to break. For this reason, a very soft material is never brittle. Brittleness is generally a very undesirable property. Burned ceramic materials which are brittle have usually been fired at too high a temperature, but some under-burned bricks are brittle if the vitrification has not been carried sufficiently far to bind the particles into a hard strong mass.

Brittleness may also be caused by cooling articles too rapidly, this treatment producing a large number of minute cracks which render the articles weak. Brittleness may also be caused by using a kiln with a damp foundation. Some firebricks are said to be brittle because crystals have formed in them during the burning period and also because of improper treatment during cooling them through the " critical

range," whilst some ceramic materials are brittle when heated on account of their coefficient of expansion. Silica, magnesia, and bauxite bricks are very liable to crack and spall when heated quickly on account of the volume changes which occur during rapid heating and cooling. When heated for a long period, fused silica tends to become brittle on account of its recrystallisation or devitrification.

There is no reliable means of measuring brittleness; the best available is to investigate the effect of blows, applied in various ways, on the material (see " Impact Tests," near the end of the present chapter).

Friability is the property which enables a material to yield readily when subjected to a crushing or abrasive force (p. 138). It is a typical characteristic of dry, sandy loams and of the soft, sandy bricks known as " rubbers " which are largely used in decorative architecture, particularly in the south of England. These bricks are so rich in sand that they have little cohesion and when two of them are rubbed together they are rapidly " worn away." Most dry clays are very friable, but they lose this characteristic when heated to redness. Clays which, when dry, cannot easily be crushed or " rubbed away " are known as " indurated " or hardened clays; many shales, fireclays, and slates are indurated clays.

Malleability is the property which enables a material to change its shape without breaking or cracking when it is passed between a pair of rollers, or is subjected to a series of blows from a hammer or similar appliance. It is especially evident in such metals as gold, silver, and copper, but is equally characteristic of plastic clays and other pastes, though as these materials are soft it is not necessary to " hammer " them. Malleability is due to the structure of the material being such that the particles can roll over each other without losing contact. It is an important characteristic of most ceramic pastes, but is usually referred to as " plasticity " (see Chapter VI).

Ductility is the property which enables a material to be drawn or pulled into any shape; it also enables a material to be extruded through a small aperture at the end of the vessel containing it. This property enables bricks, pipes, and other articles to be extruded through a " mouthpiece " attached to the end of a pugmill, " stupid " or pipe-press, the extruded material being afterwards cut into pieces of suitable length by means of taut wires on a frame. Articles so produced are said to be made by the " wire-cut " process. Although ceramic pastes are conveniently treated by this means, they are not nearly so ductile as some metals, such as gold, silver, copper, and some varieties of brass. The ductility of clays and allied materials is usually regarded as part of their " plasticity " (see Chapter VI).

Extensibility is closely related to ductility (*q.v.*) and is expressed by the greatest increase in length which can be obtained in a mass without fracturing it. The extensibility is usually determined by measuring the distance between two points or fine lines marked on a test-piece made of the material, then applying a sufficient tensile force to break the material; the two pieces are carefully fitted together and the increase in length between the two marks previously made is noted. The result may be conveniently expressed as a percentage of the original length of the test-piece. In order that the results may be comparable, all the test-pieces should be of the same shape and size. A cylindrical rod, about 9 inches long with a diameter of 1·128

inch and, therefore, a cross-sectional area of exactly 1 square inch, is convenient. The ends may be enlarged to facilitate the test-piece being firmly held in the tensile machine. The " dots " or lines used as fiducial marks may be 4 inches apart. Sometimes the extensibility is measured on the test-piece used for determining the tensile strength, but it is often more convenient to use a longer test-piece and to apply the tensile force more slowly than when making determinations of the tensile strength.

The extensibility of a ceramic material is seldom determined, as such materials are seldom used under tension. It is chiefly of value in determining the plasticity of a paste by Zschokke's method (see Chapter VI), as this investigator regards plasticity as measurable by the product of the extensibility by the tensile strength.

Elasticity is the property which enables a material to be drawn out or bent and to assume its original shape as soon as the flexile or tensile force is removed. The extent of deformation possible under these conditions is limited with each material, and when a greater force is applied, the material may either retain the distorted shape or it will break.

Elasticity is not usually of much importance in connection with clays and other ceramic materials, for, although some of them show a very slight elasticity, it is so extremely small as to be of little consequence and in most cases it cannot be measured accurately. The chief exception to this is met with in glazes, for on this property—though still more on their extensibility (p. 142) and tensile strength (p. 140)—depends the extent to which a glaze will adhere properly or will craze or peel. It is extremely difficult to adjust the contraction of a glaze and body so that both are exactly the same, yet if this is not done the glazes will not quite " fit " the body upon which it is placed, and if the glaze is deficient in extensibility, elasticity, and tensile strength, the results—cracking, crazing, or peeling—may be serious. According to Rieke, the importance of the elasticity of a glaze is often exaggerated, and the greater importance of its extensibility and tensile strength is often overlooked.

Flexibility is that property which enables a material to be bent without breaking it. Plastic clays and ceramic pastes possess a moderate degree of flexibility (otherwise " handles " could not be made by bending a roll of paste), but this property is generally regarded as part of the " plasticity " (Chapter VI). Fired ceramic materials are seldom flexible, except to a small extent when at a high temperature near their softening point. Torsional flexibility, even to a minor extent, is desirable in some electrical insulators made of porcelain or stoneware, but under ordinary circumstances the flexibility of fired ceramic wares is neglected.

Toughness is the property which enables a material to resist tensile, crushing, and other disruptive forces. It is difficult to represent it by any single figure or test, as it depends on a variety of factors, the importance of which differ on different occasions. Thus, under some conditions, toughness may be synonymous with flexibility, under others with tensile or crushing strength or, in the case of some materials at high temperatures, it may be due to the viscosity of the semi-molten binding agent.

It is usually at a maximum in materials which have great cohesion, together with some flexibility or elasticity, and at a minimum in rigid materials, as the latter are

liable to be brittle (p. 141). Toughness is commonly, but inaccurately, measured by the "Rattler test" (p. 200), which chiefly measures the resistance to abrasion, though a hard material of a brittle nature which is not easily abraded will give a low result in the Rattler test, thus showing that toughness, or its converse brittleness, do affect the results of that test. Toughness may be regarded as due to a combination of (*a*) resistance to being drawn out, and thus is the converse of ductility; (*b*) resistance to flexion and torsion, and thus is the converse of flexibility; and (*c*) resistance to impact, and thus is the converse of brittleness. It is also related to hardness and viscosity. A property which is related to so many others is highly complex in its nature and almost defies accurate definition or measurement.

According to L. Ogden [1] the toughness of porcelain is increased by increasing the proportion of flint and decreasing that of the felspar, whilst the proportion of clay is kept constant, or alternatively, if the proportion of felspar is kept constant, an increase in the proportion of flint and a decrease in that of clay will increase the toughness. Hence, the toughness of porcelain is dependent on the proportion of flint present, the strongest porcelains containing about 35 per cent.

Deformability is the property which enables the shape of a mass to be altered by the application of a force or combination of forces. It is not a simple property and cannot be determined as such, but is the converse of the transverse, impact, and torsional strengths of the material, and varies according to the means used for deforming the mass.

H. and F. Le Chatelier [2] found that substances may undergo successively three types of deformation: (*a*) elastic deformation, which is entirely removed when the deforming force is released; (*b*) a subpermanent deformation, which disappears gradually after the removal of the deforming force; and (*c*) a viscous deformation, which does not disappear when the deforming force is removed.

The deformability of a material is best estimated from a comparison of the effect on it of the various forces just mentioned.

The **crushing strength** of a material is the resistance which it offers to compression. It is often of great importance and is the kind of strength which is chiefly desired in most ceramic materials, especially those which in the fired state are used for constructional purposes, as they are often required to withstand a considerable pressure exerted by the materials above them. In order that a ceramic material may have a high crushing or compressive strength, (*a*) it must have a good binding agent which is present in sufficient amount to bind the particles of aggregate together; (*b*) the grains must interlock sufficiently, especially if the proportion of bond is small; and (*c*) the individual grains of aggregate must have great density and crushing strength, as porous particles are usually weaker. The crushing strength is, therefore, closely related to the texture of a material. These factors are considered more fully on p. 151.

Clays and other materials in a soft, plastic state show no end point when subjected to compression between two opposing plates, the sides of the sample being quite

[1] *Trans. Amer. Cer. Soc.*, **13**, 395 (1911).

[2] *Comptes Rendus*, **171**, 695–9 (1920).

free, so that such materials have no definite crushing strength. The crushing strength of dried materials appears to be very variable, but it is an advantage to know it when the materials or articles are to be piled on top of one another in a store, dryer, or kiln, as it is then possible to avoid spoiling them by piling them too high. Apart from this, a knowledge of the crushing strength of dried materials is of minor importance.

The compression or crushing strength of fired materials is often an important factor as regards their suitability for their intended purpose. In many cases, the crushing strength of the cold material is of small interest, but that of the material at the highest temperature at which it is likely to be used may make all the difference as to its suitability for some purposes (see p. 163).

In addition to its direct use, the crushing strength of a ceramic material is also an indication of the uniformity of the heat-treatment to which the material has been subjected in the burning or firing process. If several pieces made of the same material and in the same manner are found to vary greatly in their resistance to compression, it may usually be concluded that the temperature in various parts of the kiln is far from uniform, those parts being the hottest which produce the strongest samples. The determination of the crushing strength requires a powerful machine (p. 195); for many purposes, a determination of the modulus of rupture or transverse test (p. 197) is equally satisfactory and is easier to execute in the absence of a crushing machine.

According to H. Le Chatelier and B. Bogitch, the modified Brinell test described on p. 135 may be used as a substitute for the crushing test as the results are comparable, whilst the Brinell machine has the advantage of being more rapid, accurate, portable, and cheaper to use than a crushing press.

The **transverse strength** or **modulus of rupture** of ceramic materials is often of great importance and, as it may be determined with very simple apparatus, determinations of it are increasing in popularity. It appears to be closely related in many ways to the crushing strength, though the two are by no means identical. The crushing strength is the resistance offered by a material to a given pressure; the transverse or cross-breaking strength is the resistance offered by a piece of the material of unit-cross-section area to a crushing or cutting force.

The *modulus of rupture* is calculated from the transverse strength by means of the formula shown on p. 197. The transverse strength undoubtedly gives a better indication of the resistance of a material to compression than does its tensile strength, although the latter is, in many cases, closely related to it.

Comparative determinations of the transverse strength of materials in various stages of production are very useful in preventing losses during manufacture. Thus, J. E. Sproat [1] found that the loss of biscuit ware in a pottery decreased from 7 per cent. to 3·5 per cent. when the cross-breaking strength of the dry body-mixture was increased from 200 to 300 lbs. per square inch. They are also useful in comparing the strengths of slabs, tiles, thin paving bricks, pottery, saggers, etc., in order to increase their durability.

According to Bleininger and Howat, the transverse test of a dry mixture of clay and sand is a better indication of its plasticity than the tensile or compression tests.

[1] *J. Amer. Cer. Soc.*, **5**, 588 (1922).

It is, however, unwise to place much reliance on the assumed relationship of any " strength test " of a dry material with its plasticity.

A comparison of the transverse strength of saggers and other hollow-ware subject to irregularly distributed loads often enables articles of a better quality to be produced.

In considering these various kinds of " strength," it will be seen that for most purposes an article on ceramic material must possess a combination of two or more of these qualities, the ones required depending on the purpose for which the article or material is to be used. Thus, the plastic raw paste used for making articles must be readily deformed or shaped and must, therefore, have a low cohesion so as to allow the paste to move relative to each other, and yet the material must possess ductility and malleability (or plasticity), together with sufficient tensile, compressive and transverse strength to prevent fracture when the shape of the mass is altered. On the other hand, a finished article must usually have a high degree of cohesion to enable it to retain its shape under the conditions to which it is likely to be subjected, and it should also possess such properties as toughness and should not be brittle.

Factors affecting Strength

Many factors affect the strength of ceramic materials, the most important of which may be grouped under the following heads :—

(*a*) The chemical composition of the material.
(*b*) The physical properties of the material.
(*c*) The mode of preparation of the material.
(*d*) The mode of manufacture of the article.
(*e*) The conditions of drying.
(*f*) The conditions of burning.
(*g*) The temperature at which the article or material is used, or at which its strength is determined.
(*h*) Other conditions to which the article or material is or has been subjected, including weathering, sudden changes of temperature, prolonged heating, etc.

The strength of raw clay will depend chiefly on factors (*a*), (*b*), and (*h*), and chiefly on the second ; the strength of a dried clay will depend on factors (*a*) to (*e*) ; the strength of freshly-burned products on (*a*) to (*g*) ; whilst the strength of articles which have been in use for some time may be further complicated.

In order to ascertain the effect of these various factors upon the strength of ceramic materials they should first be studied separately, and afterwards in combination.

The **Chemical Composition** frequently has a very important effect on the strength of ceramic articles, but care must be taken not to exaggerate its influence ; in the past there has been a tendency to attach undue importance to the chemical composition and to neglect the physical characteristics of the materials.

The chemical composition of the raw or dried materials is of less importance, as in such materials chemical reactions take place very slowly, if at all, at ordinary

room temperatures. When the materials or articles made of them are heated to such a temperature that chemical reactions can take place, the chemical composition of the material begins to play an important part.

Most finished articles made of ceramic materials consist of solid particles of "aggregate" united by a glassy bond, the nature of the latter largely determining the strength of the article at various temperatures. As the bond is usually produced by the combination of the binding agent with some of the constituents of the aggregate, the strength of the mass also depends on the amount of bond present and on the total proportion of fluxes which are present in the raw materials. In a cold ceramic mass, the greatest strength will usually be found in the material containing the largest proportion of fluxes, such as soda, potash, lime, magnesia, etc., provided the ware has been fired at a sufficiently high temperature to render the fluxes effective. At high temperatures, on the contrary, the larger the proportion of fluxes, the lower will be the strength of the mass, because at a high temperature the bond produced by the fluxes will be soft and mobile and, therefore, unable to impart the necessary rigidity to the material. When the temperature is reduced sufficiently for the molten glassy matter to become solid, the strength of the material as a whole will greatly increase as the solid glassy matter forms a strong bond.

The effect of the chemical composition on the strength of a ceramic material is shown in the case of bricks made of *lime*; these are extremely weak, as no suitable bond can be found for them. Other non-plastic materials, such as bauxite, when attempts are made to shape them without an added bond, are very weak, but if a suitable bond, such as clay or lime is used, very strong bricks and other articles can be made, some bricks bonded with lime having a crushing strength of 10,000 lb. per square inch. Some magnesia bricks (especially those containing about 5 per cent. of ferric oxide or its equivalent) are very strong when cold, chiefly on account of the proportion of fusible matter present. On the other hand, some silica bricks are weak because of the poor quality and small proportion of lime used in making them. Table XXXVI, due to Phillipon,[1] shows the effect of varying the proportion of lime on the strength of silica bricks burned at 1300° C.

TABLE XXXVI.—*Effect of Lime on Strength of Silica Bricks*

Per cent. Lime.	Crushing Strength, kg. per sq. cm.		
	White Quartz, Central Plateau.	Normandy Quartz.	Pas de Calais Sandstone.
0	50	110	..
0·5	172	208	147
1·0	278	270	220
1·5	310	290	253
2·0	304	287	263
2·5	262	252	257

[1] *Rev. de Métal.*, **15**, 51 (1918).

Articles made of clay owe their strength when in the moist and dry states chiefly to the plastic material present, but in the fired or burned articles the plasticity is destroyed and the strength of the articles is then largely dependent on the proportion of active fluxes present. These fluxes combine with the free silica present and form glossy molten silicates. Blue bricks and other similar vitrified articles contain a larger proportion of active flux than red bricks and are, consequently, stronger. Blue bricks, tiles, etc., are particularly interesting in this respect, as the amount of glassy bonding material is not due so much to the total metallic oxides present, as to the fact that the chief of these oxides (iron) is reduced to the ferrous state by the mode of burning adopted (see p. 103) and so is converted into an active flux. Under oxidising conditions it would be largely inactive.

E. C. Hill,[1] has found that fluorspar and magnesium carbonate, either together or separately, lower the strength of terra-cotta ware, whilst whiting and furnace slag do not appreciably affect it. This difference in behaviour has not been explained, except on the assumption that fluorspar and magnesium carbonate form viscous fluids which are largely immobile, whilst whiting and furnace slag are much more mobile and "penetrating."

The effect of fluxes on the transverse strength of terra-cotta is shown in Table XXXVII, due to E. C. Hill.

TABLE XXXVII.—*Effect of Fluxes on the Strength of Terra-cotta*

	Modulus of Rupture.
	Lbs. per sq. in.
Terra-cotta clay	1518
+ 5 per cent. Maine felspar	1486
+10 ,, ,,	1905
+ 2·5 ,, powdered glass	1489
+ 5·0 ,, ,,	1687
+ 2·5 ,, white lead	1372
+ 5·0 ,, ,,	1461
+ 1·25 ,, cryolite	1339
+ 2·5 ,, ,,	1426
+ 1·25 ,, whiting	1618
+ 2·5 ,, ,,	1503
+ 5·0 ,, ,,	1545
+ 2·5 ,, Fluorspar	1275
+ 5·0 ,, ,,	1326
+ 1·25 ,, magnesium carbonate	1269
+ 2·5 ,, ,, ,,	1240
+ 5·0 ,, ,, ,,	1152
+ 5·0 ,, furnace slag	1361
+10·0 ,, ,,	1407

[1] *J. Amer. Cer. Soc.*, **5**, 832 (1922).

Fireclay bricks increase in strength in the cold with an increase in the proportion of fluxes, but, as previously mentioned, their strength at high temperatures is lessened by the addition of fluxes or of free silica (sand). E. Sieurin and F. Carlsson [1] found that 60–70 per cent. of silica gave the weakest samples. An excess of alumina is also harmful, a sudden drop in the softening point occurring with a mixture containing between 70 and 80 per cent. of alumina. If more than 80 per cent. of alumina is present and the mixture is carefully made, its softening point increases gradually with the alumina added.

Bleininger and Brown [2] consider that there is a certain relation between the composition of fireclays and their crushing strength or resistance to load at high temperatures, and have stated that most ceramic materials containing more base than corresponds to the formula 0·225 RO $Al_2O_3 2SiO_2$ (see Chapter VIII) cannot withstand a pressure of 50 lb. per square inch at a high temperature, and that an excess of silica reduces the strength of the mixture, unless it is accompanied by a reduction in the proportion of base present. Thus, when 4·4 molecules of silica were present to 1 molecule of alumina, a material failed under a pressure of 50 lb. per square inch at 1350° C., even though only 0·17 RO were present.

Lime greatly reduces the strength of fireclay bricks under load, even when only small proportions are present. According to E. Sieurin and F. Carlsson, a rapid fall is occasioned in the softening point with less than 1 per cent. of lime, beyond this proportion the fall continues, though less rapidly. Magnesia acts in a similar manner, the most rapid fall in the softening point being in silica bricks with between 0 and 0·25 per cent. With greater percentages of base, a more gradual decrease occurs. Iron oxide greatly reduces the strength of fireclay bricks at high temperatures, particularly in a reducing atmosphere. The softening point under load is rapidly decreased with less than 6 per cent. of iron oxide. This strength at a high temperature is not very much affected with percentages between 6 and 12, but beyond this it is again rapidly lowered.

Other substances besides those commonly regarded as fluxes may affect the strength of clays and refractory materials. In a complex chemical substance or mixture, such as those used for making fireclay goods, the respective proportions of the constituents may greatly affect the strength. Thus, the presence of an excess of bone ash in china ware increases the brittleness of the ware. Peters [3] found that carborundum, up to about 45 per cent., increased the tensile strength of fireclay rapidly, but larger proportions had the opposite effect, as the strength decreased with great rapidity. With some mixtures of ball clays and 70 per cent. of carborundum the maximum tensile strength is obtained and the compressive strength is also increased.

Bricks made of a mixture of bauxite and sand are much weaker than those made wholly of bauxite, on account of the different natures of the constituents. Sand expands on heating, whilst clay and bauxite shrinks, so that the strains set up on

[1] *Brit. Clayworker*, **30**, 262 (1921–22).
[2] *Trans. Amer. Cer. Soc.*, **13**, 210 (1911).
[3] *J. Amer. Cer. Soc.*, **5**, 181 (1922).

firing reduce the strength of the finished articles. O. L. Kowalke and O. A. Hongen found that the addition of silica materially increased the crushing strength of magnesia bricks at high temperatures, whilst alumina, chrome oxide, titanium oxide, and zirconia have a similar effect, though not so marked.

Chrome bricks, containing 14 per cent. of clay, are not so strong as those made entirely from chrome ore, and chrome bricks bonded with chalk are very weak.

The crushing strength of fused silica is appreciably increased by the addition of 1 per cent. of zirconia.

The effect of *water* on the strength of ceramic materials is described on p. 154, and the effect of *electrolytes* on p. 155.

The effect of chemical composition is also considered in Chapter IX.

The **physical properties** of ceramic materials has a very important influence on their strength. The chief physical properties to be considered are (*a*) the size and shape of the article ; (*b*) the texture of the material ; (*c*) the porosity ; (*d*) the coefficients of expansion or contraction ; and (*e*) the adhesive power of the bond.

Size and Shape.—The crushing strength is to some extent dependent on the size of an article or mass, and usually the larger an article the greater will be the total power required to crush it, though it need not necessarily have a high crushing strength, as the latter is expressed in terms of unit area (lb. per sq. inch). The shape has an important effect on its strength, for if it is designed badly it may be unduly weak in certain parts and so bend or crack when subjected to a great stress. For instance, sharp corners and sudden changes in the thickness of an article are sources of weakness, and, where possible, these should be avoided. The apparently abnormally great strength of hollow columns as compared with solid ones is well known and it is worthy of note that perforated bricks are stronger in proportion to their area than solid ones, as shown in Table XXXVIII, due to Professor Tetmaier.[1]

TABLE XXXVIII.—*Perforated* v. *Solid Bricks*

Crushing Strength, tons per sq. ft.		No. of Holes.	Diameter of Holes, in.
Solid Bricks.	Perforated Bricks.		
276	411	14	0·6
161	178	12	0·7
147	149	12	1·0
130	154	10	0·7
202	238	14	0·8
329	383	14	0·8

Seger also found that a solid and a perforated brick made from the same material had crushing strengths of 315 and 504 tons per sq. foot respectively.

[1] *Brit. Clayworker*, **29**, 22 (1920–21).

Texture is concerned with (*a*) the shapes and sizes of the individual particles, and (*b*) the arrangement and size of the pores or interstices between the grains. In ceramic materials, the maximum strength is obtained by the use of irregular angular grains of numerous sizes, which interlock freely; rounded grains produce a weak mass as they cannot interlock properly. Thus, bricks made of powdered calcined flint or of sea-sand are usually weak, because the grains are rounded and, consequently, do not hold well together. The strength of a ceramic mass, both in the dried and fired state, usually increases with the fineness of the grains, but an excessive proportion of fine grains is undesirable, as H. Ries [1] has shown (Table XXXIX) that it decreases the tensile strength of dried clays in a similar manner to a large proportion of large grains, such as coarse sand.

TABLE XXXIX.—*Effect of Grain-Size on Crushing Strength* (*Ries*)

Diameter of Grains.	Percentage of Grains of each Size.				
	Clay 1.	2.	3.	4.	5.
mm.					
0·005–0·0001 . .	87·96	30·645	22·00	44·00	59·00
0·01 –0·005 . .	6·95	14·210	5·66	7·11	11·00
0·25 –0·01 . .	3·00	5·585	26·55	24·35	14·70
0·5 –0·25 . .	1·00	6·400	11·45	7·80	3·50
1·0 –0·5 . .	..	42·950	33·44	16·35	11·40
Tensile strength (lbs. per sq. in.) . .	20	105	289	297	453

On the other hand, for articles requiring to possess great resistance to compression at high temperatures, H. J. Knollman [2] considers the presence of a considerable proportion of fine material to be an advantage, and various investigators have shown this to be the case with silica bricks. Thus, the effect of the grain-size on the strength of silica bricks, burned at 1300° C., is well shown in Table XL, due to Phillipon.[3]

The size of the grains of grog in fireclay mixtures has an important influence on the resistance of the fired material to transverse loads at high temperatures. Large ceramic slabs or other articles which are required to carry heavy loads should be made of comparatively coarse material. Various investigators are agreed that about 50 per cent. of grog of sizes corresponding to 4–20-mesh should be used and all fine materials should previously have been removed from it. This is also recognised in the Standard Specification for Retort Material, etc.

[1] *Trans. Amer. Cer. Soc.*, **6**, 79 (1904).
[2] *J. Amer. Cer. Soc.*, **4**, 759 (1921).
[3] *Rev. de Métal.*, **15**, 51 (1918).

TABLE XL.—*Effect of Grain-Size on Crushing Strength*

Diameter of Grains.	Compressive Strength, kg. per sq. cm.		
	French White Quartz. Central Plateau.	Normandy Quartz.	Allier Amorphous Silica.
0·05	250	300	210
0·06	140	230	80
0·07	50	150	25
0·08	23	80	5
0·09	14	55	..
0·10	8	37	..
0·12	5	20	..
0·14	3	10	..
0·16	..	5	..
0·18	..	4	..

The strongest ceramic mass consists of a suitably graded mixture of angular grains of various sizes selected so as to produce as compact a mass as possible and provided with a sufficient amount of binding material to cover each particle of aggregate and to unite them together. The production of graded aggregates of this kind is described on p. 32. The proper interlocking of the particles of aggregate is of very great importance, and the low transverse strength of many fireclay and other slabs is due to their being made of badly-graded mixtures. Similarly, the strongest burned material consists of a mass of interlocking crystals formed *in situ* and united by a glassy cement. Such a mass is stronger and more compact than can be obtained by any artificial means of assembling the particles.

It should be observed that the texture of a mass is not always uniform in every direction on account of the method used in shaping it. Thus, if a tile is made by applying pressure to its upper and lower surfaces, its structure when laid flat will not be quite the same as that when it is on edge. Hence, in all machine-made products, and to some extent with hand-made ones, the structure varies in different directions, and this should be taken into consideration when investigating the strength of an article.

Further information on texture will be found on p. 27.

Porosity.—The size and arrangement of the pores in a ceramic mass affect its strength, inasmuch as the larger and more numerous are the pores, the thinner must be the enclosing " walls " of solid material. Hence, a highly porous material—if the pores are large—must be very weak. When the pores are extremely small, their effect on the strength of the material is less noticeable.

In many fired ceramic materials, the tensile and crushing strengths are roughly

inversely proportional to the porosity. Thus, if certain bricks having a porosity of 6–12 per cent. have a crushing strength of 7000–15,000 lbs. per square inch, other bricks of a similar character, but with a porosity of 14–25 per cent., will probably have little more than half the strength of the former ones. This proportionality does not always hold, however, and A. V. Bleininger [1] has found that when the porosity and the crushing strength of numerous clay and shale bricks examined by him were plotted as a graph, the latter consisted of two portions, namely, an almost straight line indicating a gradual increase in strength with a decrease in porosity down to 3–4 per cent., and then a steep curve indicating a rapid increase in strength for lower porosities. The relation must clearly depend to a great extent on the structure of the bricks. The relation between the porosity and crushing strength of ceramic materials at high temperatures has not been sufficiently fully examined to permit very definite conclusions being drawn. Such conclusions, when based on a small number of samples, are often misleading, and when ceramic materials of different composition are examined no general conclusions seem possible; thus M. F. Beecher [2] has found that some fireclay bricks made by him, with a porosity of 51·8 per cent., suffered less deformation when heated under pressure at high temperatures than several commercial fireclay bricks having a porosity of less than 20 per cent.

In ceramic materials of a non-argillaceous character, it appears that great strength is incompatible with high porosity, though there is only a very indefinite relation between the porosity and strength of such materials (see also p. 74).

Power of the Bond.—In ceramic materials, four types of bond occur: (*a*) bonds of a plastic nature, such as clays; (*b*) bonds of an adhesive nature, such as glue, dextrin, molasses, etc.; (*c*) bonds of a hydraulic nature, such as mortar and Portland cement; and (*d*) glassy bonds such as occur in vitrified ware.

Each of these bonds increases the strength of the mass as a whole, though to very different extents and in very different ways.

A *plastic agent*, such as clay, possesses a peculiar binding power (p. 141), whereby it is able to extend its plastic properties to limited proportions of non-plastic materials which may be mixed with it, and when the mixture is dried and afterwards burned, the mass becomes stronger than before, although it has lost its plasticity.

Shales and indurated clays produce masses which are weaker in the raw and dried state, but develop great strength on firing, so that the strength finally attained may not be greatly different from that reached by more plastic clays and non-plastic material. The chief difference in this respect is that whilst plastic clays will develop great strength when heated to a relatively low temperature (900°–1000° C.), lean clays must be heated to a higher temperature (1200°–1600° C.), so that they undergo considerable vitrification in order to attain the same strength.

An *adhesive*, such as glue, tar, viscous mucilage, dextrin, flour or starch paste, heavy mineral oils, cellulose or molasses, forms a coating around each of the particles and so unites them together. The resultant mass will be moderately strong when dry, but as such adhesives are destroyed by heat they can only be used to a limited

[1] *Trans. Amer. Cer. Soc.*, **12**, 564 (1910).
[2] *J. Amer. Cer. Soc.*, **2**, 336 (1919).

extent in connection with ceramic materials. The addition of 1 per cent. of dextrin, according to H. W. Douda,[1] increases the crushing strength of dry clay from 16–52 per cent., depending on the nature of the clay.

A *hydraulic bond*, such as Portland cement, lime, etc., behaves like an adhesive, so far as the dried materials are concerned. On heating the mixture, the hydraulic bond is usually converted into a glassy bond.

A *glassy or vitrified bond* consists of a glass- or slag-like mass of molten material which, when the ceramic material containing it is at a sufficiently high temperature, melts and flows into the interstices between the solid particles. At that stage the mass as a whole is weak, but when it has cooled and the bond is solidified, an extremely strong bond is obtained. A glassy bond can seldom be used when the material is in the moist or dried state—unless water-glass (a sodium silicate) is included in this type of bond—as it only becomes adherent when fused and afterwards allowed to solidify.

In most ceramic materials, the glassy bond is produced when the articles are in the kiln and, consequently, such materials only attain their maximum strength after they have been " burned " or " fired." The formation of a vitrified bond is described on p. 160 and in Chapter XIII.

The **mode of preparation** of ceramic materials often has a very important influence on the strength of articles made from them.

The **grinding** of the materials determines the sizes and shapes of the various particles and so directly affects the strength of the mass (p. 151).

The **amount of water** present or added to the material largely influences the strength of the mass, both directly in the damp material and indirectly in the dried and fired product.

When less water is present in the ground raw material than will form a thin film around each particle, the addition of a further quantity of water will increase the strength of the material. When each particle is completely surrounded by a film of water of the required thickness, the addition of further water will effect a reduction in the strength and an increase in the fluidity of the mass.

A deficiency of water is usually preferable to an excess in the preparation of ceramic materials.

The effect of using a variable proportion of water in the manufacture of silica bricks containing $1\frac{1}{2}$ per cent. of lime, the whole material being ground to 200-mesh, is shown in Table XLI, due to M. Phillipon.[2]

Further information on the effect of water will be found in Chapter VI in the section on " Water of Plasticity," and in Chapter VII.

The **proportion of added materials**, such as the bonding agent, etc. (p. 153), may seriously affect the strength of the prepared material. It is considered later with respect to various substances.

Sometimes a very small proportion of an added material will have a very marked effect on the strength of the product. This is particularly noticeable in the case of

[1] *J. Amer. Cer. Soc.*, **3**, 885 (1920).

[2] *Rev. de Métal.*, **15**, 51 (1918).

electrolytes, which, when added to clay in the form of pastes and slips, considerably increase the strength of some dry and fired goods made from them, though few figures have been published which show the actual increase.

TABLE XLI.—*Effect of Amount of Water on Strength*

Water, per cent.	Compressive Strength after drying, kg. per sq. cm.	Compressive Strength after burning at 1300° C., kg. per sq. cm.
15	12	180
16	13	195
17	15	190
18	15	220
19	17	250
20	19	265
21	20	270

H. G. Schurecht [1] has found that the presence of some electrolytes had an important effect on the strength of dried clay, the following substances increasing the strength, in the order shown :—

(*a*) Sodium hydroxide, which may quadruple the strength of a clay paste. The addition of 0·8–2·5 per cent. of alkali was the most effective.

(*b*) Sodium silicate.

(*c*) Sodium carbonate.

(*d*) Tannic acid.

(*e*) Calcium hydroxide.

H. W. Douda [2] has found that the addition of 1 per cent. of sodium hydroxide increased the dry strength of a stoneware clay by 79·22 per cent. on the unground material, and nearly trebled it after wet grinding. A flint clay which showed a modulus of rupture of 305 lbs. per square inch, after wet grinding with plain water had its modulus of rupture increased to 439 lbs. per square inch when the material was ground with a 1 per cent. solution of sodium hydroxide.

Further information on the effects of electrolytes will be found in Chapter VI.

The **method of mixing** ceramic materials has a very great influence on the strength of the products. If, as is often the case, the mixing is incomplete, the strength of the articles will vary in different parts of their structure. The process of " pugging " is a far less effective method of mixing than " tempering " the material in an edge-runner mill with revolving pan (the so-called wet-pan mill), though pugging is much cheaper than tempering. H. W. Douda [2] has found that by tempering a

[1] *J. Amer. Cer. Soc.*, **1**, 201 (1918). [2] *Ibid.*, **3**, 885 (1920).

stoneware clay for 2 hours in a wet-pan mill, he increased its strength by 74 per cent. when dry and doubled its strength when burned at Cone 2. Similarly, the modulus of rupture of a dried flint clay was raised from 35 lbs. per square inch to 305 lbs. per square inch after tempering the wet material for two hours in a wet-pan mill. Similar increases in the strength of the dried goods were obtained with several different materials.

The *time* occupied by the mixing or tempering process also has an important effect on the strength of the product. Not only is a sufficient period of mixing or tempering very necessary to secure a uniform mixture of the materials, but it will also be found that imperfectly mixed ceramic materials are a constant source of annoyance and loss. On this subject, also, little information has been published respecting clay wares, but Table XLII, due to R. M. Howe and W. R. Kerr,[1] shows the effect of the time of tempering on the strength of the silica bricks.

TABLE XLII.—*Effect of Tempering on Strength of Silica Bricks*

Time of Tempering, mins.	Modulus of Rupture, lbs. per sq. in.
10	440
15	446
20	499

The difference is much greater with clays than with non-plastic materials.

Ageing.—When a plastic material has been mixed, its preparation is not finished; it should, if possible, be set aside for several days in order to " age " it.

This " ageing " of clay pastes has an important effect, as it appreciably increases the strength of the product, especially in the dry state, by securing a more even distribution of the water present and facilitating the retention of the colloidal matter in the mass. The period of rest during which the material is " ageing " may vary from a few hours, which has an appreciable effect for some clays, to the period of a century or more, which is reputed to be the length of time which the ancient Chinese kept their pastes prior to using them for the manufacture of china and porcelain. It is seldom practicable to allow more than a fortnight for ageing brick and tile clay, but for much coarse pottery a shorter period may suffice. An adequate period for " ageing " is almost essential to the production of retorts, glass-pots, and crucibles of best quality, as all these articles are required to stand severe conditions when in use.

The effects of ageing are not so marked with non-argillaceous materials, though still apparent. For further information on " ageing " see Chapter VI.

[1] *J. Amer. Cer. Soc.*, **5**, 164 (1922).

Effect of Shaping on Strength.—The method of shaping articles has an important influence on their strength. Hand-moulded articles are seldom as strong as machine-made ones, provided the machine is of a suitable character for the material. It is not always easy to ensure the suitability of the machinery, as so much depends on apparently trivial properties in the material. Thus, in making articles by extrusion or expression, a defective die or mouthpiece puts an excessive strain on the column of clay as it issues from the opening and so the material may crack. The cracks may not be serious and sometimes are not visible when the articles are in the freshly-made state, but during drying and firing, cracks or other defects may develop and seriously weaken the goods. A laminated structure is sometimes imparted to a column of clay made by extrusion ; it is usually due to lack of sufficient space between the bridge which carries the knives of the machine and the end of the mouthpiece, but it may also be due to the lamellar structure of the original clay (p. 22).

The various methods of shaping ceramic articles afford many other opportunities for reducing the strength of the material. Thus, if they are shaped by compression in a press which does not apply a uniform pressure over the whole surface, the resulting article will be subject to internal strains and will have a low strength, no matter how great a pressure may be applied to some parts of it.

When the pressure is applied uniformly, its amount affects the strength of the product. Under normal conditions, the greater the pressure applied the greater will be the strength of the article produced. Thus, Table XLIII, due to Watkin,[1] shows the effect of the pressure applied in producing tiles by compression of an almost dry clay-dust on their tensile strength.

TABLE XLIII.—*Effect of Pressure on Strength*

Pressure, lbs. per sq. in.	Tensile Strength, lbs. per sq. in.	Pressure, lbs. per sq. in.	Tensile strength, lbs. per sq. in.
4000	1400	2000	850
3750		1750	850
3500	980	1500	960
3250		1250	960
3000	1150	1000	940
2750	..	750	810
2500	1060	500	790
2250	1060		

The effect of the method of manufacture upon the strength of bricks is well shown by the following figures due to Emery and Bradshaw,[2] who found that lime-bonded,

[1] *Trans. Eng. Cer. Soc.*, **17**, 111 (1917–18).
[2] *Loc. cit.*, p. 132.

hand-made silica bricks had a crushing strength of 1630 lbs. per square inch, whilst bricks made of the same material by power-driven presses had a crushing strength of 2270 lbs. per square inch. Bricks of each type were heated slowly to 600° C., maintained there for one hour and then withdrawn from the furnace and allowed to cool in air. Their respective average crushing strengths before and after reheating were—

	Before.	After.	Decrease in crushing Strength, per cent.
Machine-made bricks . .	2270	2080	8·5
Hand-made bricks . . .	1630	1050	35·5

Bricks, tiles, etc., which are pressed and afterwards repressed are improved in appearance, but reduced in strength, unless exceptional care is taken to ensure their being exactly the right size, so as just to fill the box of the repress. If an article is too small, its shape will be altered in the repress and its structure will be disturbed by the second pressing. If the article were not quite homogeneous—and mechanically pressed ones tend to laminate—it would be less homogeneous after repressing it and, therefore, more liable to crack or break when subjected to any sudden stress.

Effect of Drying on Strength.—The manner in which articles made of clay and allied materials are dried has a great influence on their strength when in the dry and also in the fired state. To avoid rupture, all materials having plastic or kindred properties must be dried under conditions which will permit the water to be removed at a uniform rate throughout the mass and without the formation of an impervious skin or crust through which water from the interior of the mass cannot penetrate. The necessity of drying under suitable conditions (see Chapter VII) is particularly great with articles containing a large proportion of plastic clay, as these are specially liable to form a hard surface-skin which, at a later stage in the drying, is very liable to crack under the pressure of the water vapour which cannot escape through it, as the partly-dried material is very weak and cannot withstand the strains produced in it by the pressure of water vapour in the interior and by the uneven contraction. Joints in the articles are usually very weak at this stage, and so need special care in drying, and also when drying articles which vary greatly in thickness in different parts. When articles are dried before being placed in the kiln it is often desirable not to remove the whole of the water, as this causes them to become very friable and difficult to handle without rubbing the edges and fine mouldings, and so causing irreparable damage. A very small proportion of water is sufficient to overcome this difficulty.

Materials consisting largely of plastic clay increase in strength and rigidity when

dried slowly and, under favourable conditions, the more thorough the drying the greater is the crushing strength. For this reason, an article which has been air-dried at ordinary room temperature may have only about half the strength of a similar one which has been dried at 110° C. The difference in strength is due to the small proportion of moisture still left in the air-dried product, which enables the material to retain some of its original mobility.

The difference in the strength of clay wares when dried at different temperatures was investigated by C. W. Saxe and O. S. Buckner,[1] and is shown in Table XLIV.

TABLE XLIV.—*Variations in Tensile Strength of Clays according to Mode of Drying* (*Tensile Strength in lbs. per sq. in.*)

Clay.	Air Dried.	Dried at 55° C. for 24 hours.	Dried at 110° C. for 24 hours.	Dried at 110° C. Cooled in Desiccator.
Ball clay . . .	57·5	59·4	63·4	130·5
Ball clay . . .	32·9	34·9	38·7	69·8
Ball clay . . .	30·1	32·5	35·4	65·8
Plastic clay . . .	65·3	69·9	77·1	107·4
Ball clay . . .	49·7	52·1	54·5	85·5
Plastic clay . . .	58·9	59·8	54·4	83·3
German crucible clay .	64·1	70·6	76·1	87·9
American crucible clay .	52·6	61·2	62·0	107·2
Slip clay . . .	46·1	51·2	57·3	79·2

The effect of cooling the completely dried material in a desiccator so that it cannot absorb moisture from the air during cooling is appreciable. It is shown in the last column of the Table.

The strength of wholly non-argillaceous materials increases to some extent during the drying, but when fully dry they are not usually so strong as articles containing clay, because they do not contain either so much or so strong a bond. In most cases, such materials are much more porous than those containing clay, so that the moisture escapes more readily and the shrinkage is much less. There is, consequently, little liability of damage by rapid drying, as the stains which may occur in clay ware do not arise. For this reason, non-argillaceous materials may usually be dried quite satisfactorily at a fairly rapid rate.

Effect of Burning on Strength.—The conditions to which ceramic articles are subjected in the kiln forms one of the most important factors in determining their final strength. If they have been heated at a sufficiently slow rate, so as not to crack

[1] *J. Amer. Cer. Soc.*, **1**, 113 (1918).

them, they will be much stronger after firing than in the plastic or dry state, the final strength depending chiefly on (i) the nature and amount of the bonding material produced during the heating; (ii) the particles of aggregate united by the bond; and (iii) the better consolidation of the grains of material which result from the shrinkage of the material during the firing.

The *bond* affects the strength of the fired material after the latter has been allowed to cool, because the bond is, as its name implies, the agent which unites the other particles together. Consequently, the stronger the bond and the larger the proportion of it present, the stronger will be the articles. For this reason, vitrified masses —in which all interstices between the particles of aggregate are filled with the bond —are stronger than porous ones; the vitrified material not only contains a larger proportion of bond, which unites the other particles together more securely, but the bond itself also possesses great intrinsic strength. Clays containing at least 6 per cent. of ferric oxide, or its equivalent, when fired in a reducing atmosphere, form a strong product, because the reduced iron oxide acts as a flux, combines with the clay and so produces a mobile fluid of fused matter which penetrates and fills the pores (see Chapter XIII). When the same clays are fired in an oxidising atmosphere, the oxidised iron oxide does not fuse, and the small proportion of fused material formed does not fill the pores, so that a weaker and less vitrified article is produced. Porcelain, china, stoneware, and other articles of a vitrified nature are all much stronger than porous materials.

Magnesia bricks, when cold, are very strong, their strength being probably due to the proportion of fluxes present and the high temperature at which they are fired.

Most refractory materials cannot have their strength developed to the maximum mentioned above, because sufficient bond cannot be formed at the highest temperatures commercially attainable at present.

The *aggregate* affects the strength of an article according to the strength of the individual grains of which it is composed (see p. 151), unless these grains are porous and are completely saturated with the bond, in which case their strength may be increased.

The *shrinkage* which a material undergoes in firing affects its strength as described on p. 158, but if the shrinkage is excessive it may reduce the strength of the finished article on account of the large amount of rearrangement which the particles undergo during the heating and shrinking; this is particularly the case with mixtures which are heterogeneous in character and are deficient in vitrified bond. When a large amount of vitrification occurs, greater changes in the volume of the material may take place without decreasing the strength, though an excessive amount of vitrification must be avoided or deformation or cracks may result. The maximum strength in a fired mass is usually obtained when the amount of vitrified material or bond is just sufficient to fill the pores and to unite all the individual unfused particles, but there is not enough to separate these particles from each other to an extent which allows them to slide or slip apart. For further information on shrinkage see Chapter XIII.

The *temperature attained in the firing* affects the strength of the finished and cold

articles, because it determines, to a large extent, the amount of fusible matter or bond produced, and this, in turn, controls the strength of the mass. The effect on the crushing strength of firing materials at various temperatures is shown in Table XLV, due to Saxe and Buckner [1] :—

TABLE XLV.—*Effect of Firing Temperature on Crushing Strength of Clay*

Clay.	Room Dry. 20° C.	55° C.	110° C.	200° C.	325° C.	575° C.	825° C.
Ball clay . . .	61	89	125	110	111	195	221
Ball clay . . .	38	60	62	76	84	126	163
Ball clay . . .	36	59	66	73	78	129	158
Plastic clay . .	89	114	134	129	133	151	468
Ball clay . . .	61	80	94	98	103	151	266
Plastic clay . .	85	107	125	121	119	184	322
German crucible clay	86	91	114	127	141	253	331
American crucible clay .	73	104	145	145	153	255	294
Slip clay . . .	14	19	24	17	19	9	24
Slip clay . . .	57	75	88	80	87	92	274

It will be observed that the strength of clays from 110° C. up to about 325° C. is practically constant. During the period of decomposition of the clay (500° C.) the strength of the materials mentioned increases quite rapidly except in the case of the two slip clays, where the decomposition has little effect on the strength. It is unfortunate that these investigators did not extend their tests to include clays fired at all temperatures up to those at which loss of shape occurs.

The lack of strength in many bricks, saggers, etc., is due to the fact that insufficient care is taken in firing them. Some saggers, for example, are merely placed in a kiln with other goods and burned at the same rate as the latter, with the result that the temperature to which they are heated is not sufficiently high to produce the maximum attainable strength. If such saggers were fired independently to a higher temperature their strength would be considerably increased, though the cost of this additional firing must not be overlooked.

Table XLVI, due to R. M. Howe and W. R. Kerr,[2] shows the effect of the temperature in the burning on the modulus of rupture of silica bricks.

The *rate of firing* in the kiln also affects the strength ; if too rapid it may cause cracks or " bloating " in the articles, both of which are a distinct source of weakness.

[1] *Loc. cit.*, p. 159.

[2] *Loc. cit.*, p. 156.

TABLE XLVI.—*Effect of Firing Temperature on Modulus of Rupture of Silica Bricks.*

Temperature of Burning.		Average Modulus of Rupture, lbs. per sq. in.
Seger Cone.	° C.	
11	1320	303
14–15	1410–1435	368
16–17	1460–1480	444
17	1480	572
18	1500	533
19	1520	514

The *duration of the firing* also affects the strength of the articles when cold, because prolonged heating at a sufficient temperature produces an increase in the proportion of fusible bonding material equal to that formed by a shorter heating at a higher temperature (see Chapter XIII). Hence, it is not only necessary for the final temperature attained in the burning to be sufficiently high, but in many cases it is equally necessary to maintain the kiln at that temperature for a sufficient time to enable the maximum strength of the contents to be developed. This is especially the case with porcelain (also with silica and magnesia bricks) in which special reactions must occur before the maximum strength is obtained, but it is also important with many other ceramic materials.

The *atmosphere* in which the goods are fired may influence the strength; some, such as red bricks, firebricks, and most refractory materials are fired, as far as possible, in an oxidising atmosphere, as this ensures a material which will have the greatest strength at high temperatures, but if some of the same materials (which contain ferric oxide or its equivalent) were fired in a reducing atmosphere, their strength, when cold, would be greatly increased, because of the larger proportion of bond formed (see p. 148). A reducing atmosphere greatly reduces the resistance of refractory materials, and of most ceramic materials containing ferric oxide, to load at high temperatures.

The *cooling of the kiln* or oven also affects the strength of the contents, as too rapid a cooling may produce fine cracks or " dunts " in the ware. Articles made of silica, magnesia, and vitrified ware are particularly sensitive in this respect, and articles made of them, therefore, should be very carefully cooled after firing. The cracks produced are frequently so small as to escape notice, when the articles are immediately withdrawn from the kiln, but they greatly reduce the strength of the ware.

With some materials, such as most clay products, the actual rate of cooling need not be detrimental if it is effected by passing a large volume of air, at a temperature

only slightly below that of the contents, through the kiln. The cracks and other defects attributed to rapid cooling are chiefly due to the great difference between the temperature of the articles and that of the air admitted to the kiln. In other materials, however, the rate of cooling is important, especially where a critical range of cooling has to be passed through, as in the case of silica and magnesia ; the rate of cooling must then be regulated so as to effect all the necessary physical or chemical changes desired and yet prevent any undesirable ones. Such regulation can only be learned by constant inquiry. An investigation of the critical range of cooling of various porcelains and other ceramic materials would probably result in a decrease of the total time required for cooling the kilns and would also reduce the proportion of cracked and dunted ware.

Repeated changes of temperature, especially in the case of refractory materials, gradually reduces their strength to an extent depending on (*a*) the coefficient of expansion or contraction of the material, and (*b*) the chemical and physical changes which may take place during the repeated heating and cooling. Materials such as silica and magnesia, which are very sensitive to sudden changes in temperature, soon lose so much of their strength as to become useless unless carefully treated (see also Chapter XIII).

Repeated Heating.—When fireclay and grog bricks are repeatedly heated to a high temperature, their resistance to blows is reduced ; this reduction is attributed by Mellor and Austin to—

(*a*) The volatilisation of alkalies and silica, which results in a reduction of the mechanical strength.

(*b*) The irregular contraction of the mass as a result of the presence of irregular patches of crystals formed by chemical reactions, which occur on repeatedly heating the material.

(*c*) Crystallisation which occurs when clays are repeatedly heated at temperatures above 800° C. for long periods of time.

The ordinary burning period is not sufficiently long to effect any appreciable amount of crystallisation in firebricks, but when the heating at high temperatures is prolonged for long periods, crystallisation, with formation of sillimanite, frequently occurs. The recrystallisation of quartz as cristobalite and tridymite, and of magnesite as periclase are described in Chapter VIII.

The effect of repeated heating and cooling on quartz glass or " fused silica " is very slight, provided the temperature does not exceed 1120° C., but, according to a report by the National Physical Laboratory, prolonged heating at 1188° C. causes a slight, though not serious, diminution of strength after eight hours. About 45 per cent. of the strength is lost on heating for only four hours at 1350° C. For this reason, fused silica ware should not be heated for any long period to a temperature above 1200° C.

The **temperature during use** has an important influence on the strength of ceramic materials, because their strength is usually much lower at high temperatures. They retain their original (cold) strength until a temperature is reached at which the bonding material begins to soften and yield under pressure, or at which, as

previously mentioned (p. 147), the fluxes present in the material begin to form compounds which soften or fuse and so decrease the strength of the mass at the high temperature to which it is exposed. In this way, fluxes play a double part, as they reduce the strength of a ceramic material at high temperatures and increase it at lower ones. Sometimes the reverse is the case and the addition of what appears to be a flux actually increases the strength of the fired material. Thus, O. L. Kowalke and O. A. Hongen have found that the addition of $7\frac{1}{2}$ per cent. of silica to magnesia bricks increases the temperature at which they fail under a load of 66·5 lbs. per sq. inch from 1680° to 1870° C. Such a case is quite unusual and is difficult to explain satisfactorily.

The strength of refractory materials when hot is often more important than the strength when cold, as the latter is usually ample, whilst the former is not merely lower, but is often an unknown factor. Moreover, as the strength when cold is usually much greater than the strength when heated, any material which is sufficiently strong at the highest temperature attained during its use, is almost certain to be perfectly satisfactory at ordinary temperatures.

As most ceramic materials are not quite pure, they do not usually possess a sharply-defined softening or yielding point when heated, and consequently their crushing strength diminishes gradually over a long range of temperature; this is still more noticeable if the material be subjected to a considerable pressure or load which is not intense enough to crush the cold material, but causes it to rapidly lose its shape when any softening of the bond or other fusible constituent occurs. If the material under examination consists of a single pure substance, such as pure silica, however, the strength remains fairly constant until the fusion-point is reached and loss of shape then occurs suddenly, especially if the material is under pressure.

That the long range of temperature through which some materials lose strength progressively is due solely to the gradual production of fused or partially fused material is clearly shown by varying the pressure applied to the material, when it will be found that loss of shape occurs at a lower temperature when the pressure is greater and *vice versa*. When only a very small amount of mobile material has been formed a much greater pressure is required to deform the mass and to cause the unfused particles to move through or in the fused portion. As the temperature increases, or the time of heating is prolonged, more and more fused and mobile material is formed and less pressure is needed to move the remaining particles.

The fact that most ceramic materials have a much lower strength at high temperatures than when in the cold state, is very important in connection with their use in the construction of furnaces, retorts, crucibles, and other refractory articles. It clearly shows that at temperatures and pressures approaching the critical point it is much safer to use a single substance of a comparatively simple nature, like silica, rather than a complex material such as fireclay. In commercial use, however, attention must not be unduly concentrated on this one factor, for others, such as the great sensitiveness of silica to sudden changes in temperature, are also important. Moreover, it is often preferable to use a material like fireclay, which, as a result of its long-softening range, gives ample warning of its gradually diminishing strength,

rather than a material such as very fine silica, which collapses somewhat suddenly and with little or no warning.

The loss of strength of fired ceramic materials with a gradually increasing temperature has been investigated by V. Bodin,[1] who found that some refractory materials, such as fireclay, bauxite, carborundum, corundum, silica, and zirconia, decrease in strength when heated up to about 800° C., but increase in strength rapidly at temperatures between 800° and 1000° C. At temperatures above 1000° C., their strength, in most cases, decreases gradually. These observations are in agreement with the fact, long known to users of the large crucibles employed in the manufacture of "crucible steel," that the strength of such crucibles when they are at a bright-red heat is greater than at ordinary temperatures, though at still higher temperatures the strength is gradually reduced on account of the softening of the fusible matter present in the materials of which the crucibles are made or absorbed by the crucibles during use.

Bodin found that the strength of bricks made of magnesite and chromite decreases gradually up to the highest temperatures and does not show any increase at 1000° C. This distinguishes these two materials from the others examined by him.

Loss of strength at high temperatures may also be due to physical or chemical rearrangements of the constituents of the mass. Thus, A. S. Watts [2] has suggested that the softening of fireclay bricks at about 1300° C. when under pressure sometimes may be due to a period of weakness, coinciding with the formation of sillimanite, this being analogous to the period of weakness in silica bricks when the quartz changes to cristobalite or tridymite. This appears to be confirmed by the fact that some defective fireclay saggers show an important amount of crystal development. When sufficient sillimanite is formed, the strength of the material is increased.

Articles made of carborundum decrease in strength at a temperature of about 1200° C. on account of the partial oxidation of the carborundum with the formation of free silica and carbon dioxide. The decomposition is arrested when a film of silica is formed over the surface, thus preventing further oxidation.

The loss of strength at high temperatures may also be due to structural defects developed during the heating of the material, either (*a*) as a result of original defects, or (*b*) as a result of changes effected by the conditions of heating.

The *ratio of strength at low temperatures to that at high ones* may be calculated, in the case of fireclay products, from the following formula :—

$$\text{Bending temperature} = Ce^{-kw}$$

proposed by J. W. Mellor,[3] where C denotes the bending temperature (in Seger cones) without any load, w the pressure applied in lbs. per square inch, e is the exponential constant, and k a numerical constant depending on the nature of the clay, the method employed in making the test pieces, etc. ; it varies from 0·003 to about 0·02.

[1] *La Céramique*, **23**, 177–184 (1920).
[2] *J. Amer. Cer. Soc.*, **3**, 450 (1920).
[3] *Trans. Eng. Cer. Soc.*, **15**, 117 (1916).

G. A. Loomis,[1] on the contrary, considers that there is no definite relationship between the strength and refractoriness of fireclay bricks at high temperatures, though he found that bricks having a softening point lower than Cone 28 would not withstand a pressure of 40 lbs. per square inch at 1350° C.

It appears impossible that any simple formula can be used to express the relation between the strength of fireclay bricks, etc., at high temperatures to that at ordinary temperatures, as such a relation must be dependent, to a large extent, on the texture of the articles. Thus, very fine-grained bricks usually have a smaller relative strength at high temperatures than coarse-grained, open bricks, because the latter are not so readily affected by the fluxes present. Fine-grained bricks, on the other hand, are more dependent on the films of fused matter between the grains, because at high temperatures the materials forming these films, whilst not sufficiently softened to flow freely, are viscous enough to permit the deformation of the mass.

Effect of Weathering on Strength.—Exposure to weather greatly decreases the strength of most ceramic articles, those composed of clay which has merely been dried being the most affected. Table XLVII, due to Gebauer,[2] shows the compressive strength of air-dried clay bricks and the effect on them of constant contact with a moist atmosphere.

TABLE XLVII.—*Effect of Moisture on Strength of Dry Clay.*

Nature of Bricks.	Compressive Strength, kg. per cm.²	
	Air Dried.	After 4 weeks' Storage in Contact with Moist Air.
Machine-made . .	42·3	27·2
,, . .	34·9	21·1
Hand-made . .	30·9	21·3
,, . .	26·1	20·1

Most building bricks and roofing tiles are very resistant to weathering, but this is not the case with firebricks. Table XLVIII, due to Howe, Phelps, and Ferguson,[3] shows the effect of exposure on the strength of refractory bricks.

It will be seen that the cold fireclay bricks lost from 1–21 per cent. of their crushing strength after six months', and 11–28 per cent. after twelve months' exposure. One brand of specially strong machine-made bricks was found to withstand six months'

[1] *U.S. Bur. Stand. Tech. Paper*, 159 (1920).
[2] *Tonind. Ztg.*, **44**, 301–3 (1920).
[3] *J. Amer. Cer. Soc.*, **5**, 109 (1922).

exposure to the weather practically without loss in strength. Some very porous hand-made fireclay bricks are greatly reduced in strength on exposure and may be made practically worthless after six months' exposure.

TABLE XLVIII.—*Effect of Exposure on Crushing Strength of Bricks*

Type.	Strength.	As Received.	After 6 Months' Exposure.	After 12 Months' Exposure.
Fireclay brick A .	Maximum	1418	1404	1109
	Minimum	782	855	891
	Average	1127	1114	1005
	Per cent. deviation	22·8	13·4	9·3
Fireclay brick B .	Maximum	1355	909	755
	Minimum	545	545	545
	Average	885	693	640
	Per cent. deviation	26·9	20·5	10·1
Silica brick . .	Maximum	2727	2245	1418
	Minimum	1373	1327	909
	Average	1830	1680	1111
	Per cent. deviation	23·1	17·7	17·5
Magnesia brick .	Maximum	5582	4255	3914
	Minimum	3273	2726	2082
	Average	4464	3780	2978
	Per cent. deviation	14·5	12·7	17·4

Silica bricks may lose as much as 39 per cent. of their crushing strength when cold if they are exposed to the weather for twelve months, whilst magnesia bricks decrease in crushing strength by 15 per cent. after six months' exposure and 33 per cent. after twelve months' exposure. The strength of magnesia bricks when heated under load is also affected, some bricks, after being weathered for twelve months, failing, under a pressure of 25 lbs. per square inch, at a temperature of 40° C. lower than new bricks. Magnesia bricks are more seriously affected by the weather than almost any other kind of refractory brick and much greater care is therefore required in their storage.

Effect of Frost on Crushing Strength.—The crushing strength of articles is reduced by subjecting them to the action of frost, as shown in Table XLIX, due to J. C. Jones.[1]

[1] *Trans. Amer. Cer. Soc.*, **9**, 567 (1907).

The effect of freezing does not appear to be related to the original strength of the brick, but to depend upon other factors such as texture, porosity, temperature, and duration of burning, etc. Some curiously contradictory results are sometimes obtained when the crushing strengths of bricks, etc., which have been repeatedly subjected to freezing, *e.g.* in a refrigerator, are determined.

TABLE XLIX.—*Effect of Freezing on Crushing Strength*

Kind of Brick.	Hardness.	Crushing Strength.		Per cent. Loss in Strength.	Per cent. Pores Space.
		Frozen.	Unfrozen.		
Plastic surface clay	Soft	1194	1374	13·1	33·0
	Med. Soft	3567	3400	4·6 [1]	26·9
	Med. hard	4289	5315	19·9	21·2
	Hard	7377	7260	1·6 [1]	10·2
Plastic shale . .	Soft	2671	2913	8·6	26·2
	Med. soft	4625	5793	20·2	17·8
	Med. hard	8522	10143	16·5	11·6
	Hard	7606	11470	33·8	5·8
Wire-cut shale .	Soft	3729	4637	19·6	27·6
	Med. soft	6965	8117	14·2	17·1
	Med. hard	9165	11315	19·4	2·1
	Hard	11500	11997	4·1	0·9

Articles composed of uniform grains appear to be more resistant to frost than those composed of various-sized grains, as in the former the water is more easily distributed when expansion occurs as a result of the water freezing. Thus, a uniform-grained brick may have a porosity of 20 per cent. and not burst when frozen, whereas one with only 5 per cent. porosity may be destroyed if its texture is irregular. This statement has been contradicted by Purdy and Moore,[2] who consider that an article composed of particles having the greatest range of sizes of grains, and consequently of pores, has also the greatest resistance to frost.

According to J. C. Jones,[3] a hard, brittle brick requires a greater force to disintegrate it than a softer brick, but the distance through which the force must act is smaller, as the former cannot be strained to the same extent as the latter without failure. For this reason, vitrified bricks require a greater force to commence

[1] Increase.
[2] *Trans. Amer. Cer. Soc.*, **9**, 704 (1907).
[3] *Ibid.*, 536.

disintegration, but when once the destruction is started it proceeds more rapidly than with softer and more porous bricks.

Hard bricks are often less resistant to frost than softer ones on account of the pores, though small, being rigid and having a small elastic limit, so that they are unable to stand much strain when a force is applied. There is, however, no definite relation between the hardness of bricks, etc., and their resistance to frost. J. C. Jones obtained the following results :—

TABLE L.—*Effect of Freezing on Strength of Bricks*

Extent of Burning.	Per cent. Loss of Strength.			
	Surface Clay.	Shale in Plastic State.	Wire-cut Process.	Average.
Soft . . .	13·1	8·6	19·6	13·8
Med. soft . .	4·6 [1]	20·2	14·2	9·9
Med. hard . .	19·9	16·5	19·4	18·6
Hard . . .	1·6 [1]	33·8	4·1	12·1

It will be seen that the surface clay has least resistance to frost in the medium, hard-burned condition ; the plastic shale suffered most in the hard-burned condition ; whilst the shale shaped by the wire-cut process was almost equally affected in the soft and medium hard-burned conditions.

Effect of Blows in Reducing Strength.—The crushing strength of most ceramic materials is greatly reduced by subjecting them to repeated blows.

Effect of Deposited Carbon on the Strength.—The deposition of carbon on and in the pores of fireclay articles is very detrimental to their strength, both at low and high temperatures, on account of the decomposition of the clay which appears to occur as a result of the catalytic action of the carbon. The diminution in strength is most serious in retorts which are used for the distillation of carbonaceous materials. Carbon does not appear to have the same effect on highly siliceous materials.

Effect of Slags and Flue-dust on Strength.—The prolonged subjection of any ceramic articles to the action of molten slags greatly reduces the strength of the articles, especially at high temperatures. If the articles are porous they absorb the molten slag, and Nesbitt and Bell [2] found that, after such penetration, the crushing strength of some red-hot silica bricks was reduced from 1451 lbs. per square inch to 775 lbs. per square inch. Denser bricks would have a less penetration and, consequently, the crushing strength would be less affected.

[1] Gain.

[2] *Proc. Amer. Soc. Test. Mat.*, **19**, 619–39 (1919).

Strength of Clays and Clay-products

The strength of various ceramic materials depends on the factors mentioned on pp. 146–169. In some cases, the strength is a very important characteristic, but in others it is not so important and may be sacrificed to secure other properties.

Strength of Raw Clay and Clay Pastes.—The strength of raw clays and clay pastes, *i.e.* of clays in the plastic state, varies very greatly. Some lean clays will break under a tension of a few ounces, whilst other highly plastic clays may withstand a tension of several pounds per square inch. The duration of the application of the force also affects the result, as a small force acting throughout a long period will have an effect similar to that of a much larger force acting for a much shorter time. As the strength varies with the plasticity of the clay and on the proportion of clay and water present, no definite figures can be usefully published. Plastic clays are usually much stronger in the raw state than shales and indurated clays.

Strength of Dry Clays.—The strength of ceramic materials in the dried condition is often important, for, obviously, the dried articles must be sufficiently strong to withstand the amount of handling to which they are likely to be subjected and also the weight of any articles placed above them when they are set in the kiln. Such articles as tiles must be particularly strong when in the dry state. Some pieces of pottery also require to be made of material of considerable strength when dry.

The strength of dry clay is probably largely due to the interlocking of the grains. This appears to be confirmed by the fact that a well-graded material (p. 152) produces a stronger mass when dried than an ungraded mixture, though others consider that the strength is due rather to the cementing power of the plastic or colloidal matter in the clay.

Like clays in the plastic state, dried clays vary greatly in tensile strength; in some, it is as low as a few pounds per square inch, whilst in others it may be as high as 400 lbs. per square inch. Brick clays in the dry state have usually a tensile strength of about 100 lbs. per square inch. Clays which have the greatest plasticity when in the form of a paste usually have the greatest strength when dry.

According to H. H. Sortwell,[1] the average modulus of rupture of various ball clays when dried is as follows :—

Table LI.—*Transverse Strength of Ball Clays*

	Lbs. per sq. in.
Tennessee . . .	366
Kentucky . . .	282
Devonshire . . .	443
Dorset	405
Other English clays .	419

[1] *New Jersey Ceramist*, Mar. 1922, p. 5.

A. S. Watts [1] classifies bond clays with reference to their strength as bonds as follows :—

TABLE LII.—*Transverse Strength of Bond Clays*

	Strength of Dry Clays, lbs. per sq. in.
Low	0–100
Medium low	100–200
Medium	200–400
Medium high	400–800
High	over 800

Bleininger and Howat [2] found that the tensile strength of various American clays, when dry, varies from an average of 210 lbs. per square inch with some highly plastic ball clays to 34 lbs. per square inch with china clay. When such clays were mixed with an equal weight of standard Ottawa sand their tensile strength varied from 250 lbs. per square inch to 26 lbs. per square inch. Their results of tensile and crushing tests are shown in Table LIII.

TABLE LIII.—*Strength of Dry Clays* (*lbs. per sq. in.*)

	Without Sand.		With Sand.	
	Crushing Strength.	Tensile Strength.	Crushing Strength.	Tensile Strength.
Ball clays	565–1148	135–210	464–777	124–190
Plastic fireclays	631– 954	155–172	476–553	113–150
Shales	636– 806	126–187	403–449	77–111
Plastic kaolins	455– 539	104–147	286–559	54–110
Primary kaolins	205– 349	34– 69	164–172	29– 35

[1] *J. Amer. Cer. Soc.*, **3**, 247 (1920).
[2] *Trans. Amer. Cer. Soc.*, **14**, 274 (1914).

The transverse strengths of the American clays, examined by Bleininger and Howat,[1] varied from 558 lbs. per square inch with some ball clays to 74 lbs. per square inch with some china clays, and when mixed with half their weight of standard sand the transverse strengths were reduced to 330 and 53 lbs. per square inch respectively. Table LIV shows the average limits of strength :—

TABLE LIV.—*Transverse Strength of Dried Clays*
(*Results in lbs. per sq. in.*)

	Without Sand.	With Sand.
Ball clays . . .	375–558	242–330
Plastic fireclays . .	484–520	216–280
Shales . . .	311–403	178–237
Plastic kaolins . .	239–325	122–210
Primary kaolins . .	74–166	53– 82

The dry strength required in any one case will depend on the nature of the articles to be made. Large articles, such as bricks, do not need so strong a material, but tiles, pottery, and other thin articles require a much stronger material when in the dry state so as to avoid damaging them in handling. When tiles or other articles are made by compressing the finely ground material in the form of a powder, the dry product is very weak and has to be handled very carefully.

As the cohesive power of most materials in the raw and dried conditions is comparatively low compared with that in the burned state, most articles are very weak, and must, therefore, be very carefully handled so as to avoid damage.

Strength of Burned Clay Wares.—The strength of articles, etc., made of burned clay varies according to the materials used and the mode of manufacture, very great variations sometimes occurring in articles made under apparently identical conditions. The need for careful control is, therefore, very evident.

The strength of **building bricks** is not of such great importance as is sometimes supposed, because even a poor brick (if sound) is stronger than well-laid brickwork, because of the weakness of the mortar. Usually the bricks have at least ten times the crushing strength of the brickwork when ordinary mortar is used, but if the bricks are laid in Portland cement the strength of the brickwork is increased so that the crushing strength of the individual bricks is only $2\frac{1}{2}$ to 5 times that of the brickwork.

Table LV shows the average results of a very large number of tests made by the author on various kinds of building bricks.

[1] *Loc. cit.*, p. 171.

TABLE LV.—*Average Crushing Strength of Bricks*

	Tons per sq. ft.
London grey stocks	95
Suffolk white bricks and gault bricks	135
Essex red sand stocks	96
Leicester red bricks (wire-cut)	275
Fletton bricks	255
Staffordshire blue bricks	483
South Yorkshire (stiff-plastic process)	272
Dutch clinkers	492
Rubber bricks and cutters (very variable)	74

Table LVI shows the results obtained by two other investigators on a much smaller number of bricks of each kind.

TABLE LVI.—*Crushing Strength of Bricks*

Kind of Brick.	First Crack, tons per sq. ft.	Crushed, tons per sq. ft.	Authority.
Aylesford red, pressed	71	141	Unwin.
Rugby, common red	158	190	,,
Leicester wire-cut	115	229	,,
Manchester wire-cut	87	264	Popplewell.
,, common red	74	120	,,
"Engineering" pressed	110	290	,,
,, ,,	160	280	,,
Red shale	67	220	,,
Enfield shale, red	205	496	,,
Accrington plastic (Huncoat)	118	250	,,
Digby colliery (Notts)	248	353 [1]	Unwin.
Common blue Staffordshire	240	353 [1]	,,
Blue Staffordshire	82	356	Popplewell.
Blue brindled, Staffordshire	204	485	,,

[1] Not crushed.

It is very desirable to have official (legal) standards for the minimum strengths of various kinds of bricks, but none has yet been adopted, though the following figures have been suggested as a preliminary to further study :—

TABLE LVII.—*Suggested Minimum Strengths for Building Bricks*

	Tons per sq. ft.
Blue bricks and clinkers . . .	300
Hard-burned facing bricks . .	250
First-class common bricks . .	150
Second-class common bricks . .	90

These figures are purposely rather low, and for ordinary requirements it is desirable to specify as a minimum strengths about 30 per cent. above these figures.

The American Society for Testing Materials tentatively specifies the following for the compression strength of building bricks, the samples consisting of buff bricks, which are tested on the flat :—

TABLE LVIII.—*Strength of American Bricks*

Kind of Bricks.	Average.		Minimum.	
	Lbs. per sq. in.	Tons per sq. ft.	Lbs. per sq. in.	Tons per sq. ft.
Thoroughly dry sample .	3000	193	2500	160
Thoroughly saturated sample . . .	2500	160	2000	128
Sample after freezing for 5 hours and thawing in 1 hour, this treatment being repeated 20 times	2500	160	2000	128

The same Society also tentatively specifies the following for the modulus of rupture of building bricks, tested on the flat, the supports being 7 inches apart.

TABLE LIX.—*Transverse Strength of Bricks*

	Average.	Minimum.
	Lbs. per sq. in.	Lbs. per sq. in.
Thoroughly dry sample . . .	400	325
Thoroughly saturated sample . .	275	225
Sample after freezing for 5 hours and thawing in 1 hour, this treatment being repeated 20 times . .	275	225

The minimum crushing strength allowed in Germany for ordinary building bricks is 136 tons per square foot.

The Standardisation Committee of the German Brick Industry in Czecho-Slovakia [1] specifies the following strengths for different kinds of bricks :—

TABLE LX.—*German Specifications for Bricks*

Type of Brick.	Average Strength, kg. per sq. cm.	Minimum Strength of Single Specimens, kg. per sq. cm.
Clinker	over 500	400
Hard	,, 300	240
Ordinary	,, 150	120
Soft	,, 100	80

Note.—1 kg. per sq. cm. = 14·22 lbs. per sq. in.

Vitrified bricks are much stronger than ordinary ones, and should, therefore, be used where greater strength is required. They may also be used where the bricks are to be of greater impermeability or hardness than common bricks. The strength of blue bricks is shown in Table LXI and the English tentative specification in Table LVII.

Sewer bricks do not usually require to have an exceptional strength, but must be very impermeable. The American Society for Testing Materials specifies the following compression strengths for sewer bricks made of clay or shale :—

[1] *Allg. Ton. Zeit.*, **41**, No. 46, 1 (1922).

TABLE LXI.—*Specified Strength of Sewer Bricks (American)*

	Compressive Strength (on edge), lbs. per sq. in.		Modulus of Rupture, lbs. per sq. in.	
	Mean of 5 Tests.	Individual Minimum.	Mean of 5 Tests.	Individual Minimum.
Class A, vitrified .	5000 or over	..	1200 or over	..
,, B ,, .	5000 ,,	4000	1200 ,, .	800
Hard . . .	3500 ,,	2500	600 ,,	400
Medium . . .	2000 ,,	1500	450 ,,	300

Paving bricks are required to be strong and hard and to combine all the qualities expressed by "toughness" (p. 143). They must also be very uniform in strength, as if a soft brick is used with a number of harder ones it will be worn away more quickly and will cause a depression which will soon result in the chipping of the adjacent bricks by passing traffic. For this reason, the variation in the strength of such individual bricks should not differ much from the average strength of all the bricks used on a job. As paving bricks are subjected to repeated blows rather than to great pressure, their effective strength is best estimated from the results of the "Rattler Test" described on p. 200.

According to G. H. Brown,[1] in order that paving bricks may give good results when in use, they should not lose more than 22 per cent. of their weight when subjected to the standard "rattler test." Some bricks which he examined showed 23–27 per cent., and gave good service, but those showing a loss of more than 27 per cent. were invariably of low durability.

The National Brick Manufacturers' Association and the American Society for Municipal Improvements specify that paving bricks tested by the standard "rattler test" should never lose more than 18 per cent. of their weight and the average loss on one charge of bricks should not exceed 14 per cent. of the original dry weight.

Other specifications are shown in Table LXII.

The modulus of rupture of good paving bricks when tested by the standard cross-breaking test is 1500–3500 lbs. per square inch, the average being 2000–3000 lbs. per square inch. It will usually be found that the cross breaking strength in individual bricks varies from 8–30 per cent. on either side of the average of a large number of bricks and the usual variation is about 20 per cent. This variation is due to irregularities in the material and in the process of manufacture.

The American National Brick Manufacturers' Association specifies for paving bricks a modulus of rupture of not less than 2500 lbs. per square inch and the average

[1] *Trans. Amer. Cer. Soc.*, **16**, 364 (1914).

strength of three bricks should not be less than 2700 lbs. per square inch when tested by the standard method (p. 200).

TABLE LXII.—*Loss of Weight (per cent.) in "Rattler Test"*

	Average.	Minimum.	Maximum.
Illinois State Highway Dept. . .	23	17	27
,, ,, ,, . .	25	20	28
,, ,, ,, . .	27	23	29
Ohio State Highway Dept., 4-in. bricks	22	18	26
New York State Highway Dept. . .	24	..	..

The strength of porous clay wares, such as **porous pipes, tiles, terra-cotta,** etc., is generally about the same as that of building bricks. Articles containing a larger proportion of vitrified material are stronger, and highly vitrified ware, such as stoneware, has a strength approximating to that of blue or vitrified bricks.

Earthenware and **china** vary considerably in strength, the former being usually much weaker than the latter and the latter being usually rather weaker than other forms of porcelain.

Porcelain varies in strength according to the nature of the materials used and the mode of manufacture. W. Peaslee [1] states that ordinary felspathic porcelain has a tensile strength up to 1500 lbs. per square inch and a compression strength up to 40,000 lbs. per square inch, whilst some of the best high-tension porcelain has a tensile strength of 12,500 lbs. per square inch and a compression strength of 65,000 lbs. per square inch. A. V. Bleininger [2] also found that the compressive strength of such porcelain varies from 50,000 to 65,000 lbs. per square inch and that the usual tensile strength is about 13,000 lbs. per square inch and the modulus of elasticity about 7,000,000.

F. H. Riddle and J. S. Laird [3] found the tensile strength of 'triaxial' porcelains to be about 6249 lbs. per square inch with conical test pieces and 5760 lbs. per square inch with dumbbell test pieces. 'Special' porcelains were found to have an average tensile strength of 10,250 and 9390 lbs. per square inch respectively under the same conditions. They claim that the tensile strength of porcelain is, to some extent, a measure of the resistance to impact and that, for this purpose, it is more reliable than the compression test. E. Rosenthal [4] gives the following figures for various porcelains :—

[1] *J. Amer. Inst. Elec. Eng.*, **39**, 445 (1920).
[2] *Met. and Chem. Eng.*, **16**, 589 (1917).
[3] *J. Amer. Cer. Soc.*, **5**, 384 (1922).
[4] *Keram. Rundschau*, **29**, 81–82 (1921).

TABLE LXIII.—*Strength of Porcelains*

	Kg. per sq. cm.				Cm. drop per sq. cm.	
	Compression.	Tensile.	Torsion.	Transverse.	Impact Cross-Breaking.	Impact Compression.
Insulator body	4000–5000	..	481	590	0·90	98
,, ,,		261	500	540	0·95	105
Table ware	4000–5000	..	..	640	1·36	112
Chemical porcelain	..	..	500	410	1·23	117
Hermodorfer hard porcelain	4780	..	..	490	..	..
American hard porcelain	..	..	..	520	0·08	..
Seger porcelain	..	..	430	..	1·00	69

According to Staley and Hromatko,[1] the impact strength of the best American semi-porcelain table ware is about 0·925 ft.-lb. per cub. inch, whilst that of china ware varies from 0·638 to 0·794 ft.-lb. per cub. inch.

The crushing strength of **fireclay bricks** varies according to the temperature at which they have been burned and depends upon the extent to which the particles are bonded together with fused matter. As a general rule, the higher the temperature at which such bricks are burned the greater will be their strength when cold. In any case, firebricks should be at least strong enough to resist the weight of any superimposed structure and should usually have a crushing strength of at least 150 tons per square foot, this being the specified strength for ordinary brickwork, though the crushing strength for firebricks mentioned in the specification of the Institute of Gas Engineers is much lower than this, namely, 115 tons per square foot, or 1800 lbs. per square inch, and is only 85 per cent. of the minimum strength of common bricks permitted in Germany. Fortunately, most firebricks of good quality made in this country are stronger than the minimum just mentioned and occasionally tests have been made which showed that some firebricks have a crushing strength of 250 tons per square foot when cold.

Grog bricks are sometimes rather weaker than bricks made wholly of fireclay. This is particularly the case when a binding clay with a short range of vitrification is used, or if an insufficient proportion of binding clay has been used. There should be very little, if any, difference in the strength of fireclay and grog bricks.

The crushing strength of **fireclay bricks at high temperatures** is very important and is dependent on various factors (see p. 163). The temperature at which the bricks will lose their shape or collapse depends upon the pressure to which they are

[1] *J. Amer. Cer. Soc.*, **2**, 227 (1919).

subjected. Thus, Bleininger and Brown [1] found that fireclay bricks containing more than 0·225 equivalents of RO in the formula $x\mathrm{RO}.y\mathrm{Al_2O_3}.z\mathrm{SiO_2}$, representing the composition of the bricks, are unable to withstand a pressure of 50 lbs. per square inch at a temperature of 1350° C., and when the relation between the proportions of silica to alumina exceeds 2 : 1, the effect of the RO content is correspondingly increased. Hence, when the silica : alumina ratio is 4 : 1 an RO content of 0·17 equivalents is sufficiently high to cause the failure of the bricks at the temperature and pressure mentioned.

C. H. Lovejoy [2] has found that under a load of 50 lbs. per square inch poor fireclay bricks may begin to fail at temperatures below 1000° C. and fail completely at 1200° C. ; medium quality bricks begin to fail at 1100° C., but first-class ones show no signs of failure below 1200° C. and some are not affected at 1350° C., but all fireclay bricks fail below 1500° C.

Employing a much lower pressure, K. Endell [3] obtained the following figures for the amount of deformation sustained by various refractory bricks under a pressure of 1 kg. per square cm. (14·2 lbs. per square inch) at different temperatures :—

TABLE LXIV.—*Deformation of Fireclay Bricks at High Temperatures*

	Temperature, ° C.	Deformation, mm.
Fireclay brick . .	1300	30
Magnesite brick . .	1500	10
Silica brick . . .	1650	collapsed.
Carbon brick . . .	1720	none.

Although M. Gary, in 1910, found that fireclay bricks at 1000° C. are stronger than when cold and that at higher temperatures a reduction in strength occurs, the significance of this observation was almost completely overlooked until nearly ten years later, when V. Bodin investigated the strength of various materials at different temperatures and found that several show two points at which the strength is very low, viz., one at 800° C., and the other at 1200° C., whilst between these points—at a temperature of about 1000° C., the strength is greater than at any other temperature. It is not generally known that a great reduction in strength occurs at 800° C., but it is most important that this fact should be borne in mind in constructing furnaces, etc., which are to be heated above this temperature.

[1] *Trans. Amer. Cer. Soc.*, **13**, 210 (1911).
[2] *Chem. Met. Eng.*, **22**, 109 (1923).
[3] *Z. Stahl u. Eisen*, **1**, 1920.

Table LXV, due to V. Bodin, shows the crushing strength of various French fireclay bricks at different temperatures.

TABLE LXV.—*Crushing Strength of Hot Fireclay Bricks* (*kg. per sq. cm.*)

Brick.	20° C.	800° C.	1000° C.	1300° C.	1500° C.
A	195	125	105	740	40
CL	920	555	575	360	65
P	1110	485	1755	115	20

Fireclay bricks in which a large proportion of the clay has previously been converted into artificial sillimanite are very resistant to loads at high temperatures, and A. V. Bleininger [1] has found that a material consisting of 80 per cent. of artificial sillimanite, 10 per cent. of plastic fireclay, and 10 per cent. of kaolin when heated to 1400° C. under a load of 50 lbs. per square inch, contracted only 0·61 per cent., whilst a mixture of eighty parts of artificial sillimanite and twenty parts of kaolin contracted only 0·48 per cent. of its length.

Unanimity has not yet been reached with regard to the minimum permissible crushing strength of fireclay bricks at high temperatures and no official specification for general use in the United Kingdom has yet been published. The one usually adopted (though unofficially) is based on the recommendation of Bleininger and Brown, who consider that no fireclay brick should be considered to be of first-class quality if it shrinks more than 1 inch when placed vertically in a suitable furnace and heated to 1350° C. whilst being subjected to a pressure of 50 lbs. per square inch. The American Gas Institute specifies :

Firebricks.	Change in Volume.
First quality, Grade A.	Not more than $2\frac{1}{2}$ per cent. swelling or shrinkage when held for $1\frac{1}{2}$ hours at 1350° C. under a pressure of 25 lbs. per square inch.
,, ,, ,, AA.	Not more than $1\frac{1}{2}$ per cent. volume change in $1\frac{1}{2}$ hours at 1400° C. under a pressure of 25 lbs. per square inch.
Second quality . .	Under $2\frac{1}{2}$ per cent. change at 1300° C.
Third quality . .	Change in volume greater than $2\frac{1}{2}$ per cent. at 1300° C. or at a lower temperature.

[1] *J. Amer. Cer. Soc.*, 3, 155 (1920).

The U.S. Bureau of Standards (1914) specifies the following strengths at high temperatures for various classes of fireclay bricks :—

Quality No. 1*A* . .	When tested on end, the bricks should not shrink more than ½ inch in a standard length of 9 inches under a load of 50 lbs. per square inch at 1350° C.
Quality No. 1*B* . .	Do. do.
Quality No. 2 [1] . .	Under the same conditions of test, the brick should not shrink more than ½ inch under a load of 25 lbs. per square inch at 1300° C.

The *transverse strength* or *modulus of rupture* of fireclay articles is sometimes used instead of the crushing strength as an indication of strength, both in the cold and at high temperatures.

Hartmann and Kobler [2] give the following figures for the modulus of rupture of refractory bricks :—

TABLE LXVI.—*Transverse Strength of Refractory Bricks at High Temperatures.*

	Modulus of Rupture, lbs. per sq. in.	
	20° C.	1350° C.
Fireclay bricks (grade A) .	665	113
Silica bricks . . .	550	161
Magnesia bricks . .	1390	136
Chrome bricks. . .	1390	22

According to M. F. Beecher,[3] the transverse strength of highly porous fireclay articles made of sawdust and fireclay compares very favourably with that of denser ones, except in the case of materials of the highest porosities, as shown in Table LXVII.

[1] The standard here set is rather higher than is usual for No. 2 refractory bricks.
[2] *Trans. Amer. Electrochem. Soc.*, **39**, 129 (1921).
[3] *J. Amer. Cer. Soc.*, **2**, 336 (1919).

TABLE LXVII.—*Porosity and Modulus of Rupture.*

	Porosity, per cent.	Modulus of Rupture, lbs. per sq. in.
Mixed with sawdust. . . .	60·6	283
,, ,, ...	56·5	270
,, ,, ...	51·8	533
,, ,, ...	47·7	547
,, ,, ...	46·1	474
,, ,, ...	43·0	436
,, ,, ...	39·5	716
Siliceous clay brick (without sawdust)	32·0	304
Norton special brick ,, ,,	31·3	558
Flint clay brick ,, ,,	21·0	436

R. F. Geller [1] has found that the transverse strength of fireclay tiles decreases very rapidly as the temperature is increased, as shown in Table LXVIII.

TABLE LXVIII.—*Temperature and Modulus of Rupture*

Temperature. ° C.	Modulus of Rupture, lbs. per sq. in.
1275	245·5
1300	98·7
1325	54·2
1350	26·0
1350	33·5
1350	28·9

Slabs made of fireclay have been found by the U.S. Bureau of Standards not to be able to bear much more than their own weight at 1350° C., and if the slabs are supported in such a manner as to leave a long span between the supports, failure may occur without any load being applied to the slabs. This is due largely to the material forming the slabs being badly graded. The greatest resistance to cross-breaking is

[1] *J. Amer. Cer. Soc.*, **4**, 608 (1921).

obtained in a mass which is so graded as to reduce the proportion of voids to the minimum possible and, consequently, contains some fine material.

Resistance to impact is not often specified in connection with fireclay bricks, but the German Admiralty (1913) specifies that fireclay bricks should be sufficiently strong to be cut with a sharp hammer without breaking.

M. E. L. Dupuy [1] found that the resistance to impact of fireclay bricks at high temperatures is about $4\frac{1}{2}$ times as great as their resistance to a continuously applied load or pressure.

The strength of other solid fireclay goods should be similar to that of fireclay bricks and slabs.

Hollow refractory ware should be very strong, so as to resist the pressure of the contents at high temperatures. Thus, **crucibles** should have both a high tensile and a high crushing strength, as they are liable to be " pulled " by the weight of their contents and to be crushed by the pressure of the tongs. In order to secure the maximum tensile strength when hot, the clays used in the manufacture of crucibles should have a high-bonding power and the particles of aggregate should interlock well. The steel makers have long used for their crucibles a number of different clays in suitable proportions together with a little graphite or coke-dust, as by this means they have been able to obtain stronger crucibles than could be obtained with any of the clays when used alone. The crucibles used by steel makers are stronger when at a red heat than when cold. Crucibles which are very rich in carbon are not so strong as those composed chiefly of clay and are liable to leak when lifted out of the furnace with tongs. Very large crucibles rich in carbon are, therefore, somewhat risky to use ; small ones, being much thicker in proportion to their volume, are fairly safe.

According to A. V. Bleininger,[2] bond clays for use in making plumbago or graphite crucibles should have a modulus of rupture when tested with an equal quantity of sand of about 325 lbs. per square inch.

Glasshouse pots (used for making glass) must, like crucibles, be very strong in order to withstand the pressure of the molten glass, and those used for making plate glass must have sufficient additional strength to enable them to be lifted from the furnace after each melt and carried to the casting table on to which the glass is poured.

According to A. V. Bleininger,[2] the bond clays used for making glasshouse pots should, after being mixed with an equal weight of standard sand and dried, have a modulus of rupture of at least 250 lbs. per square inch, but M. W. Travers [3] considers that the tensile strength is more important than the compressive or transverse strength in such vessels.

Retorts require to be very strong to resist (*a*) the weight of the setting and the superimposed structure ; (*b*) the weight of the contents of the retort or the pressure they exert upon it ; and (*c*) the rough handling to which they are subjected, such as when the retorts are being filled or emptied. Determination of the crushing strength

[1] *La Céramique*, **25**, 308–10 (1922).
[2] *Bureau of Standards, Tech. Paper* **144**.
[3] *J. Soc. Glass Tech.*, **4**, 138–9 (1920).

of small pieces does not help very much in comparing the quality of various retorts and it would seldom pay to determine the crushing strength of a whole retort when heated to a very high temperature *in situ*. The greatest pressure to which retorts are usually likely to be subjected is 12–28 lbs. per square inch, which may be applied at any temperature below about 1400° C., so that if they are well made of a good quality of fireclay or silica, there need be no anxiety as to their crushing strength. When retorts collapse, it is usually due either to abnormal treatment when in use or to lack of sufficient refractoriness ; the latter—as a result of the amount of fused material which is produced—is the cause of low crushing strength at high temperatures.

Saggers are required to be very strong at the maximum temperature attained during the firing of the particular goods for which they are used, in order that, when filled, they may be piled one above another without the pressure of the upper saggers causing the collapse of the lower ones. Pieces cut from saggers usually have a crushing strength of about 1340 lbs. per square inch, but such a figure gives no indication of the crushing strength of saggers as a whole, and determinations of the crushing strength of whole saggers appear to be misleading owing to the difficulty of applying the pressure uniformly. For this reason, the transverse strength is often a better indication of the durability of saggers and other containers used at high temperatures. The results shown in Table LXIX by S. C. Linbarger and C. F. Greiger [1] were obtained from test pieces, each $2\frac{3}{8}$ in. $\times 1\frac{7}{8}$ in. cross-section, supported on 6-inch centres and tested when cold and at 1300° C.

TABLE LXIX.—*Transverse Strength of Pieces of Sagger*

	Modulus of Rupture (lbs. per sq. in.)	
	At 15° C.	At 1300° C.
A . .	1130	153
B . .	1180	457
C . .	910	405
D . .	1290	558
E . .	2740	494

These figures, like those mentioned above, do not show the strength of the sagger as a whole, but only that of the material of which it is made. They are, therefore, of very limited value, though Linbarger and Greiger claim that good saggers can be distinguished from others by test-pieces (of the size mentioned) cut from them having a modulus of rupture at 1300° C. of more than 350 lbs. per square inch.

[1] *J. Amer. Cer. Soc.*, **3**, 543 (1920).

Strength of Siliceous Refractory Materials

Owing to the low plasticity of siliceous refractory materials, other than clays (see pp. 170–184), the articles made therefrom are usually simple in shape and are well represented by *silica bricks*.

The crushing strength and transverse strength serve to discriminate between well- and poorly-burned silica bricks as well as between those with a proper and improper lime-content. The fine hair-cracks which may sometimes be noticed on the face of silica bricks do not affect, to any great extent, the strength of the bricks, as usually the cracks are quite superficial.

Sand bricks which have been hardened with steam, but not fired, are usually much less resistant to pressure than silica firebricks, on account of the size of their particles and the absence of sufficient active cement or bond.

The strength of silica bricks depends on—

(*a*) the sizes of the particles and the proportion of each size (see *Grading*, p. 151) ;
(*b*) the proportion of water used in making the bricks ;
(*c*) the proportion of lime or other bond used to bind the particles together ;
(*d*) the thoroughness of the mixing ;
(*e*) the pressure applied in shaping the bricks ;
(*f*) the temperature attained and its duration when the bricks were burned during the course of manufacture ;
(*g*) the temperature of the bricks when tested or used.

The effect of the size and grading of the particles in silica bricks is well shown by the following figures obtained by Phillipon :—

Table LXX.—*Effect of Texture on Strength of Silica Bricks*

Size of Grains.	Crushing Strength, lbs. per sq. in.
(*a*) Passed entirely through 200-mesh sieve . . .	4200
(*b*) ,, ,, ,, 80-mesh sieve . . .	1000
Mixture of *a* and *b*	3000
30 per cent. less than 200-mesh	2840–3350

Clay-bonded bricks are usually rather stronger than lime-bonded ones before burning, but the fired bricks are both about equally strong. In order to secure the maximum strength in silica bricks, it is most important that the materials should be of a suitable nature and compounded in the right proportions as well as being mixed with the bond and water to form a homogeneous paste. If the mixing is incomplete, the bricks will be weak. In any case, silica bricks are not so strong as fireclay bricks.

The Institution of Gas Engineers specifies that, when tested on end, cold silica bricks should have a compressive strength of not less than 1800 lbs. per square inch, which is a little below the average of British-made silica bricks.

Bradshaw and Emery [1] found that the average crushing strength of a number of machine-made silica bricks which they examined was 2270 lbs. per square inch, whilst the hand-made bricks they tested averaged 1630 lbs. per square inch, but this must not be understood to mean that hand-made silica bricks are necessarily weaker than machine-made ones.

According to R. J. Montgomery and L. R. Office,[2] the crushing strength of American silica bricks at ordinary temperatures varies from 900–3700 lbs. per square inch and averages 1800–2800 lbs. per square inch.

Harvard gives the following strengths for American ganister and quartzite bricks:—

TABLE LXXI.—*Crushing Strength of American Silica Bricks*

	Crushing Strength, lbs. per sq. in.		
	On Side.	On Edge.	On End.
Ganister bricks—			
Illinois	2345	1564	2119
Pennsylvania . . .	2896	1044	1551
Missouri	2370	1792	1803
Quartzite bricks, A . . .	2139	528	297
,, ,, B . . .	..	986	1588

He offers no explanation of the very great differences apparently caused by the position of the brick during the test. H. Le Chatelier and B. Bogitch [3] have suggested 100 kg. per square cm. (or 1400 lbs. per square inch) as the minimum crushing strength for good silica bricks and state that 200 kg. per square cm. (or 2800 lbs. per square inch) is a very satisfactory strength; some silica bricks examined by them had a crushing strength as high as 300 kg. per square cm., or 4200 lbs. per square inch.

At high temperatures silica bricks are stronger than fireclay bricks, as they do not soften gradually, but fail suddenly when once their softening point is reached. Good silica bricks with a lime bond will not usually collapse below 1350°–1470° C. when heated under a pressure of 50 lbs. per square inch. Where clay is also present in the bond, as in ganister bricks, they may soften at a rather lower temperature. A comparison of the strengths of silica and other refractory bricks at high temperatures, made by Le Chatelier and Bogitch, is shown in Table LXXII.

[1] *Trans. Eng. Cer. Soc.*, **19**, 73 (1919–20).
[2] *J. Amer. Cer. Soc.*, **1**, 338 (1918).
[3] *Rev. de Métal.*, **15**, 511 (1918).

TABLE LXXII.—*Crushing Strengths of Firebricks at various Temperatures*

	Crushing Strength, lbs. per sq. in.						
	15° C.	500° C.	1000° C.	1300° C.	1400° C.	1500° C.	1600° C.
"Star" silica brick .	2420	2135	1705	1065	855	680	425
Kaolin . . .	2700	2560	2985	1280	(170)	(14)	(7)
Eubœan magnesia .	5975	5405	4550	3840	3415	2630	(115)
Styrian magnesia .	2060	1850	1210	940	70	(42)	(14)

Le Chatelier [1] examined the changes in the crushing strength of "Star" silica bricks at various other temperatures, with the results shown in Table LXXIII.

TABLE LXXIII.—*Crushing Strength of "Star" Silica Bricks*

Temperature, ° C.	Crushing Strength, lbs. per sq. in.	Temperature, ° C.	Crushing Strength, lbs. per sq. in.
15	2418	1200	1209
520	2247	1320	882
670	2133	1460	711
800	1977	1540	526
950	1778	1600	427
1050	1707		

C. E. Nesbitt and M. L. Bell found that American silica bricks when heated to 1350° C. had a crushing strength of 991 lbs. per square inch for good bricks and 861 lbs. per square inch for bricks of medium quality, which is only about half that of cold bricks.

R. M. Howe [2] considers that load tests on hot silica bricks are of little value, as all good silica bricks will withstand a pressure of 25 lbs. per square inch at 1500° C. For a similar reason, the American Gas Institute does not recommend a determination of the crushing strength at a high temperature, but specifies that silica bricks and blocks should not change more than 1 per cent. in volume when subjected to a temperature of 1500° C. for 1½ hours under a load of 25 lbs. per square inch.

The *modulus of rupture* of cold silica bricks should be at least 500 lbs. per square

[1] *Rev. de Métal.*, June 1917. [2] *J. Amer. Cer. Soc.*, **1**, 347 (1918).

inch. D. W. Ross [1] has stated that silica bricks should have an average modulus of rupture of 540 lbs. per square inch and an effective modulus of 284 lbs. per square inch.

E. M'Gee [2] has found that the modulus of rupture of American silica bricks at 1350° C. is approximately one-third that at atmospheric temperature and varies between 130 and 189 lbs. per square inch.

Kieselguhr bricks when cold should have a crushing strength of about 1600 lbs. per square inch.

Some light-weight **tridymite bricks** made by Messrs J. & H. Sankey are stated by Mellor to be able to withstand a pressure of 50 lbs. per square inch at Cone 30 (1670° C.).

Silica retorts when heated to 1250° C. are stronger than those made of fireclay, as they do not soften at that temperature, but they fail suddenly at a slightly higher temperature.

Quartz glass, according to V. Bodin, has a crushing strength, when cold, of about 2550 kg. per square cm. (35,700 lbs. per square inch); on heating, the strength is reduced, as shown in Table LXXIV.

TABLE LXXIV.—*Crushing Strength of Quartz Glass*

Temperature, ° C.	Crushing Strength, kg. per sq. cm.	Crushing Strength, lbs. per sq. in.
800	1040	14788
1000	780	11092
1300	1670	23747
1500	100	1422

The presence of 1 per cent. of zirconia in quartz glass is said to increase the mechanical strength. When in the form of fine threads, quartz glass is quite elastic. Such threads are used for galvanometers, etc.

The modulus of elasticity of various kinds of glass, etc., is shown in Table LXXV.

TABLE LXXV.—*Modulus of Elasticity of Glass, etc.*

Material.	Modulus of Elasticity, kg. per sq. cm.	Authority.
Opal	3890	Auerbach.
Quartz glass	6970	,,
,, ...	6240	Schulze.
Quartz (perpendicular to axis) .	8560	Auerbach.
,, (parallel to axis) . .	10620	,,
Jena glass	4500	Schott.
,, ...	7500	,,

[1] *Bur. Stand., Tech. Paper* 116. [2] *J. Amer. Cer. Soc.*, **5**, 888 (1922).

Strength of other Refractory Materials

Chromite bricks, when properly made, are very strong at ordinary temperatures; their crushing strength is usually 2800 to 5600 lbs. per square inch, being largely dependent on the nature of the raw material and the mode of manufacture. According to M'Dowell and Robertson,[1] chromite bricks cannot withstand a heavy load at high temperatures, but fail suddenly under a load of 50 lbs. per square inch at 1450° C. Some chromite bricks, examined under that pressure by Mellor and Emery,[2] failed at 1400° C.

V. Bodin [3] found that the strength of chromite bricks remains constant up to about 950° C., and then falls rapidly, as shown in Table LXXVI.

Table LXXVI.—*Crushing Strength of Chromite Bricks*

Temperature, ° C.	Crushing Strength, kg. per sq. cm.	Crushing Strength, lbs. per sq. in.
20	450	6399
800	450	6399
1000	425	6044
1300	215	3057
1500	75	1067

Carbon bricks should have a crushing strength of at least 4500 lbs. per square inch when cold, and carbon electrodes a crushing strength of about 3250 to 5380 lbs. per square inch and a transverse strength of 700 to 1200 lbs. per square inch.

Magnesia bricks are rather stronger than fireclay bricks at ordinary temperatures, but this is largely dependent on the proportion of fluxes present, their crushing strength being usually 2000 to 6000 lbs. per square inch. Bricks which are very strong when cold are obtained when 5 per cent. of iron oxide is present, but at high temperatures, the strength is reduced as a result of the fusion of the compound formed by the flux and the magnesia. American magnesia bricks, according to M'Dowell and Howe,[4] have a crushing strength, when flat, of 5000 to 8600 lbs. per square inch; the crushing strength when the bricks are stood on edge or on end is usually 30–40 per cent. less than this. At high temperatures, the strength of magnesia bricks is rather less than that of silica bricks, no magnesia bricks being able to withstand a pressure of 50 lbs. per square inch at 1550° C. According to G. L. Brown,[5] at or near this temperature an internal change appears to take place in the magnesia, with the result that the bricks fail suddenly. Le Chatelier and

[1] *J. Amer. Soc.*, **5**, 865 (1922).
[2] *Gas J.*, **142**, 478 (1918).
[3] *Loc. cit.*, p. 165.
[4] *J. Amer. Cer. Soc.*, **3**, 185 (1920).
[5] *Trans. Amer. Cer. Soc.*, **14**, 391 (1912).

Bogitch [1] found that this change occurs at 1300–1400° C. with the poorer bricks and 1500–1600° C. in the better ones.

The strength of magnesia bricks was determined at different temperatures by V. Bodin [2] and is shown in Table LXXVII.

TABLE LXXVII.—*Crushing Strength of Magnesia Bricks*

Temperature.	Eubœa.		Styria.	
° C.	Kg. per sq. cm.	Lbs. per sq. in.	Kg. per sq. cm.	Lbs. per sq. in.
20	260	3697	450	6399
800	265	3768	295	4195
1000	230	3271	190	3002
1300	110	1564	115	1635
1500	5	71	30	457

The effect of silica on the resistance of magnesia bricks to pressure at high temperatures is, according to M'Dowell and Howe,[3] as follows :—

TABLE LXXVIII.—*Crushing Strength of Silica-Magnesia Bricks (under a Pressure of 65 lbs. per sq. in.)*

Silica.	Average Temperature at Failure.	Silica.	Average Temperature at Failure.
Per cent.	° C.	Per cent.	° C.
0	1680	7½	1870
3	1800	8	1852
6	1850	12	1838
7	1860		

Dolomite bricks are not so strong as magnesia bricks.

Bauxite bricks can scarcely be made without any additional bond, as they would be so weak ; by adding lime or clay, strong bricks can be made ; the strongest lime-bonded bauxite bricks made have a crushing strength of 10,000 lbs. per square inch ; clay-bonded bauxite bricks are rather stronger.

Bauxite bricks with a clay bond will withstand a pressure of 40 lbs. per square

[1] *Trans. Eng. Cer. Soc.*, **17**, 18 (1917–18).
[2] *Loc. cit.*, p. 165.
[3] *J. Amer. Cer. Soc.*, **3**, 185 (1920).

inch up to about Cone 33 (1730° C.), and 50 lbs. per square inch up to 1350–1500° C. According to V. Bodin [1] the strength of aluminous bricks at different temperatures is as follows :—

TABLE LXXIX.—*Crushing Strength of Aluminous Bricks*

Temperature.	Bauxite Bricks.		Corundum Bricks.	
° C.	Kg. per sq. cm.	Lbs. per sq. in.	Kg. per sq. cm.	Lbs. per sq. in.
20	395	5627	790	11234
800	270	3839	530	7537
1000	715	10167	615	8745
1300	55	782	310	4428
1500	20	284	30	427

Alundum articles have a crushing strength up to 15,410 lbs., and a tensile strength up to 1700 lbs. per square inch.

Carborundum bricks are extremely strong, both at ordinary temperatures and when heated. In the cold, the average strength is over 5000 lbs. per square inch, but some bricks with a crushing strength as high as 9650 lbs. per square inch have been made. At high temperatures, provided decomposition does not occur, bricks and other articles made of carborundum are eight to ten times as strong as those of fireclay. When heated to 1200° C. the carborundum begins to decompose and this decomposition is accompanied by a decrease in its strength. When heated in air, the carborundum becomes coated with a film of silica, as a result of which its decomposition is largely prevented and the strength is retained.

According to tests made by V. Bodin,[1] the strength of carborundum bricks increases up to 1000° C. and then decreases, as shown in Table LXXX.

TABLE LXXX.—*Crushing Strength of Carborundum Bricks*

Temperature, ° C.	Crushing Strength, kg. per sq. cm.	Crushing Strength, lbs. per sq. in.
20	415	5901
800	425	6044
1000	585	8319
1300	150	2133
1500	70	995

[1] *Loc. cit.*, p. 165.

Lime bricks are very weak, and consequently have been little used as a refractory material; no bond has yet been found which will produce lime bricks which are sufficiently strong at high temperatures.

Zirconia bricks have, according to V. Bodin,[1] a crushing strength at ordinary temperatures of 395 kg. per square cm., or 5530 lbs. per square inch; he found that on heating, their strength is reduced, as shown in Table LXXXI.

TABLE LXXXI.—*Changes in the Crushing Strength of Zirconia Bricks*

° C.	Kg. per sq. cm.	Lbs. per sq. in.
800	275	3911
1000	345	4906
1300	90	1280
1500	10	142

Mellor and Emery [2] found that zirconia bricks "squatted" at about 1600° C. under a pressure of 25 lbs. per square inch and at 1420° C. under a pressure of 75 lbs. per square inch.

THE STRENGTH OF GLAZES

The strength of glazes has not been investigated to any great extent, yet it is important in connection with the avoidance of cracks and "peeling."

The elastic modulus of stoneware glazes is generally, according to Rieke,[3] between 5700 to 6800 kg. per square mm. W. Steger [4] has found that the elastic modulus of lead glazes is lower than for leadless ones and is more strictly dependent on the chemical composition, though the variation in the moduli as determined by different observers renders it difficult to state definitely whether any real relationship exists between them.

The tensile strength of glazes is of more importance than the crushing strength. The tensile strength of stoneware glazes is, according to R. Rieke,[3] about 5 to 8 kg. per square mm., though some glazes have much lower strength and average only 3 kg. per square mm.

[1] *Loc. cit.*, p. 165.

[2] *Gas Journal*, **142**, 478 (1918).

[3] *Berichte der Technisch-wissenschaftlichen Abteilung des Verbandes keramische Gewerke*, **5**, 815 (1919).

[4] *Keram. Rundsch.*, **27**, 313–6 (1919).

Determination of Strength of Ceramic Materials

The principal methods of determining the strength of clays and other ceramic materials are naturally based on the various forms in which the " strength " of these materials is exhibited. According to the information required, a method is used which determines one or more of the following : (1) tensile strength ; (2) compression or crushing strength ; (3) transverse strength or modulus of rupture ; (4) resistance to impact ; (5) torsional strength ; (6) deformability ; (7) the " rattler " test ; (8) resistance to repeated freezing.

Some of these methods may be applied either to the cold material or to that at any suitable temperature. The strength of a material or article at the temperature at which it is used is, in many cases, of much greater importance than its strength at atmospheric temperatures. This is especially the case with refractory materials.

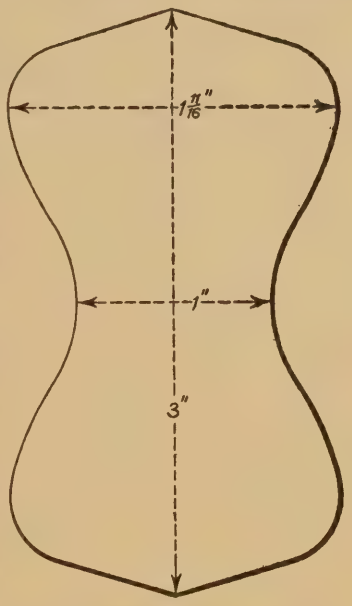


Fig. 12.—Tensile Test-piece.

Tensile Strength. — The tensile strength of ceramic materials is most conveniently determined in the same manner as that of Portland cement, though when very weak materials, such as plastic or dry clay, is being tested a lighter and more sensitive machine is preferable. The shape of the test-piece usually employed for making tensile tests is shown in fig. 12. It consists of a block of the material, the ends being $1\frac{1}{16}$ inches by 1 inch, whilst the centre is 1 inch square. The test-pieces are moulded in a brass mould or are cut from a large piece. Care must be taken in making the test-pieces and a considerable amount of skill is necessary to produce a sound sample which will break centrally and be free from adventitious air-blebs, laminations, etc., and is homogeneous throughout. Great care is also required in the drying of moulded test-pieces so as to avoid strains, especially with fine-grained clays, which are very liable to develop fine cracks and, consequently, give low results when tested.

The test-piece is placed accurately between the clips of the testing machine (fig. 13), and force is gradually applied to it—usually by shot or water, which flows into a receptacle and so operates a series of levers, or by means of a weight sliding along a beam. The rate at which the force is applied must be the same for all pieces, otherwise the results will not be comparable, the " time factor " being very important. The usual rate is 100 lbs. in twelve seconds, but for very weak specimens a lower rate may be employed.

When the test-piece breaks, the force which has been applied is ascertained, either by weighing the shot or water, or by noting the position of the sliding weight, and as the test-piece has a cross-sectional area of 1 square inch the tensile strength is at once obtained in lbs. per square inch.

It is important in making tensile tests that the samples should break in the centre, otherwise, the results will be incorrect and the test should be repeated.

Great variations frequently occur in determining the tensile strength, so that a considerable number of tests (at least ten) should be made in order to obtain an approximately accurate average result.

In making tensile tests of plastic or dry clay and similar weak materials, a simpler apparatus may be used and the test-piece may, if desired, consist of a plain cylinder

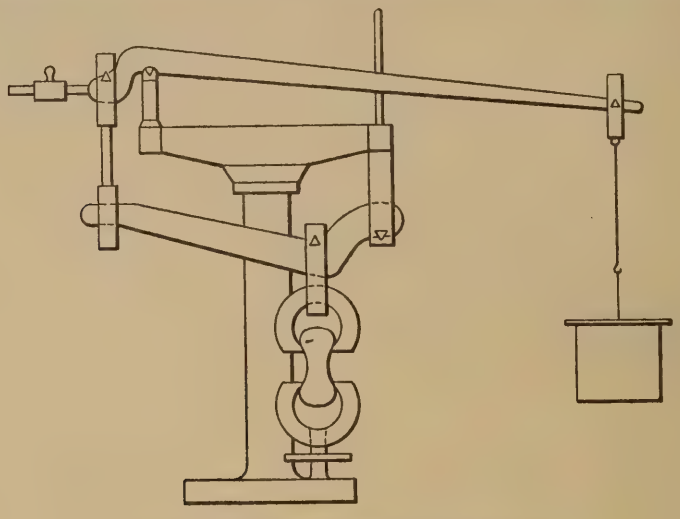


Fig. 13.—Tensile Testing Machine.

or rod 1 inch in diameter. One end of the test-piece is gripped by a rubber-lined clamp and is suspended vertically from a horizontal beam ; a second clamp is attached to the lower end of the test-piece and from this a light bucket is hung, into which shot or water is allowed to flow at a pre-arranged rate until fracture occurs. The weight causing fracture is then divided by the cross-sectional area of the test-piece, so as to express the tensile strength in lbs. per square inch.

The *extensibility* may be measured by placing the two portions of the test-piece together and measuring the increase in its length. For this purpose, it is desirable before making the tensile test to make two small dots or thin lines on the test-piece at a convenient distance apart and to measure the distance between them before and after the test. The increase in length multiplied by 100 and divided by the original length or distance between the marks will be the percentage of extensibility. The author has found that extensibility tests are preferably made on rods or cylindrical test-pieces rather than on those of the shape shown in fig. 12.

Various other methods have been devised for determining the tensile strength, one of which consists in measuring the length of a clay column which can be extruded through an aperture of a certain definite size before the column breaks. This test is conveniently made by placing the clay in a vertical cylinder with a $\frac{3}{8}$-inch aperture

in the base, and a piston with screw-down motion at the top. On turning the screw slowly and regularly the paste is extruded through the aperture and hangs vertically until its weight is greater than its tensile strength, when the column breaks. The tensile strength is found by dividing the weight of the broken piece of paste by the area of the aperture through which it was extruded.

The strength of the dried pottery is sometimes determined by means of a tensile test, but the transverse test, which is much simpler, is increasingly used for this purpose.

The **compression or crushing strength** is determined by applying a gradually-increasing pressure to a test-piece of known cross-section until it either breaks or is deformed to a certain amount which is decided upon as the end-point of the test. The rate at which the pressure is applied should be constant, or the results of different tests will not be comparable. A further disadvantage of crushing tests is that unless a carefully standardised method is employed the results are not comparable, as the strength varies according to the method used for applying the pressure, the rate at which it is applied, and the shape and size of the test-pieces. The most concordant results are obtained when cubical test-pieces are used, but for convenience whole or half bricks are frequently tested. The bricks are usually laid "flat," their cross-sectional area then being 9 inches by $4\frac{1}{2}$ inches = 40·5 square inches, but more accurate results are obtained by standing the bricks "on end."

It is very difficult to make satisfactory compression tests of bricks "on the flat" on account of the vagueness of the end point. A cube, or a prism of square cross-section whose height is one and a half times the breadth, gives much more concordant results. The German method of cementing together two half bricks so as to form a rough cube, appears to be quite satisfactory, though it has not found favour elsewhere. The Institution of Gas Engineers specifies that firebricks should be placed on edge, though this gives quite different results from those obtained when a cube is cut from the brick or when it is laid flat. The chief objection to testing bricks on edge or on end is that they are not used in this position, but this may not be serious if the only purpose of this test is to discriminate between bricks of good or bad quality.

The strength on edge bears a relation to the strength on the flat with each make of bricks, but no general rule is possible on account of the varying structure. Hence, A. V. Bleininger's [1] statement that an average ratio of the strength on the flat to that on edge 1·15 : 1 is of limited application.

For determining the crushing strength of materials in either the raw or fired state, it is generally convenient to use 2-inch cubes. Smaller samples are not usually satisfactory, as the results are not so concordant, though Zschokke and Bodin prefer to use very small cylinders.

Care should be taken that the upper and lower faces of the test-piece are smooth, perfectly parallel, and exactly at right angles to the direction in which the pressure is applied, or the pressure will not be evenly distributed. If there are any irregularities, the surfaces should be made smooth with a coat of Portland cement or plaster of Paris and pieces of stout millboard should be placed above and below

[1] *Trans. Amer. Cer. Soc.*, **12**, 568 (1910).

the test-piece just prior to crushing it. H. D. Foster [1] prefers to cover the test-pieces with a mixture of three parts of Portland cement to one part of unretarded gypsum mixed with sufficient water to form a paste.

The American Society for Testing Materials requires crushing tests to be made upon half bricks, the bearing surfaces of which are coated with shellac and the pieces bedded between blotting-paper, heavy fibrous building paper, heavy felt or, where the surface is very uneven, in plaster of Paris. As the results obtained on determining the crushing strength of a number of bricks, etc., made at the same time, and presumably of equal strength, vary considerably, it is unwise to accept the result of only one test ; an average of at least three, or preferably six, tests should be taken. The Institution of Gas Engineers specifies that the crushing strength should be taken as the average of three tests. Compression tests of plastic or dried clay should be made on twenty specimens, as the variations are often large.

The crushing strength of refractory materials at high temperatures may be determined in two ways :

(*a*) The material may be heated to the desired temperature and the crushing strength determined whilst the temperature is maintained, or

(*b*) A definite load or pressure may be applied to the test-piece, which is then heated under this pressure until a temperature is reached at which either serious distortion or collapse occurs.

The second method is the one most generally used, though it is modified in various ways. For instance, Mellor and Moore [2] measure the resistance to crushing at high temperatures by applying to the test-piece a constant load of 54, 72, 84, or 112 lbs. per square inch and increasing the temperature until a definite amount of deformation has taken place, whilst Bleininger and Brown [3] apply a constant load of 25 to 50 lbs. per square inch at a constant temperature—usually between 1150° and 1500° C. —and measure the amount of deformation occurring at the given temperature.

In the compression test suggested by J. B. Shaw,[4] the load is applied by means of a spring, the initial pressure on the cold brick or other test-piece being adjusted to 50 lbs. per square inch. As deformation occurs the pressure becomes less. In this way, Shaw's method more nearly approximates to the conditions found in industrial furnaces, because in the latter the bricks do, to some extent, adjust themselves to their surroundings.

In the load test suggested as a standard by the American Society for Testing Materials in 1917, a brick of ordinary dimensions is subjected to a pressure of 25 lbs. per square inch or 1·765 kg. per square cm. The rate of heating should be in accordance with Table LXXXII.

After the test the furnace should be allowed to cool at least five hours before removing the test-pieces. The load is calculated from the average horizontal cross-section as determined on the specimen prior to testing it.

[1] *J. Amer. Cer. Soc.*, **6**, 623 (1923).
[2] *Trans. Eng. Cer. Soc.*, **15**, 117–130 (1915–16).
[3] *Trans. Amer. Cer. Soc.*, **12**, 337–369 (1910).
[4] *Ibid.*, **19**, 498 (1917).

TABLE LXXXII.—*Heating Schedule for Crushing Test under Load*

Material.	Temperature in ° C. to be Maintained at the Time-Intervals Specified.					
	1 hr.	2 hrs.	3 hrs.	4 hrs.	4½ hrs.	6 hrs., end of Test.
Silica material . . .	200	500	900	1350	1500	1500
Fireclay, heavy duty .	500	900	1150	1300	1350	1350
,, medium ,, .	500	850	1100	1250	1300	1300
,, light ,, .	500	750	950	1050	1100	1100

Transverse tests are, for some purposes, superseding compression or crushing tests, as the former can readily be made without the use of large and expensive apparatus.

In making a transverse or cross-breaking test, the test-piece is supported upon two triangular " knife edges " and pressure is applied by means of a third knife edge on top of the test-piece, resting on a sheet of glass or steel to prevent cutting. The pressure is increased at a prearranged rate, until the test-piece breaks. The pressure at the moment of fracture is a measure of the strength of the test-piece. The modulus of rupture (in lbs. per square inch) may then be found from the following formula :—

$$M=\frac{3Pl}{2bd^2},$$

where P is the breaking load in pounds, l is the span in inches, and b and d are the width and depth of the test-piece respectively, in inches.

The cross-breaking test specified by the American Society for Testing Materials is as follows :—

" At least five bricks shall be tested, laid flatwise with a span of 7 inches and with the load applied at midspan. The knife edges shall be slightly curved in the direction of their length. Steel-bearing plates about ¼ inch thick and 1½ inches wide may be placed between the knife edges and the brick. The lower knife may rest on a wooden base block slightly rounded transversely across its top." The modulus of rupture is then calculated from the formula given above.

The American National Brick Manufacturers' Association requires the supports to be 6 inches apart. When specially moulded pieces are to be tested, they may conveniently have a cross-section 3 inches by ½ inch and a length of 14 inches, supported on knife edges 10 inches apart. The modulus of rupture of roofing tiles is usually determined on pieces of about this size.

For determining the modulus of rupture of dry clay, the American Ceramic

Society [1] specifies that the test-pieces should be made from clay dried between 64° and 76° C., screened to pass a 20-mesh sieve, then mixed with an equal weight of standard silica sand of 20–30-mesh and sufficient water; the pieces are shaped by moulding. The test-pieces are 7 inches long and 1 inch square cross-section when in the plastic state and are dried under cloths at room temperature for two days, being turned over every twelve hours to secure uniform drying, after this they should be dried for at least five hours between 64° and 76° C. and then at 110° C. until they attain a constant weight. The pieces, after cooling in a desiccator, are placed upon knife edges with $\frac{1}{4}$-inch radius, set 5 inches apart, and loaded at the rate of 100 lbs. per minute and the cross-sectional area of the bar is determined at the fractured face of the broken test-piece. The test is to be made upon ten test-pieces and the average result taken.

It is most important that the test-pieces used in the transverse test should be perfectly straight and free from flaws, otherwise unreliable results may be obtained.

The transverse strength of *pipes* is very difficult to determine, because it is not easy to reproduce in the laboratory the same stresses as occur in use. The pipes to be tested are usually supported in the same way as a brick, except that two knife edges are placed 2 feet apart and a third one supplying the pressure being placed exactly between the two. The pipe should not be placed in a cradle and tested, because in practice pipes which break are due to their not having been properly bedded in the ground.

Impact Tests are used for determining the resistance of articles which are subjected to rough handling or are liable to be struck against other articles or to be dropped. They are also applicable to domestic table ware, electrical porcelain, and other articles in which brittleness (p. 141) is objectionable. The tensile strength of materials is sometimes determined as an indication of the resistance of articles to impact, but in this respect it is not always reliable.

An impact test devised by H. F. Staley and J. S. Hromatko [2] for testing porcelain plates consists of a pendulum 24 inches long, at the end of which is a $1\frac{1}{4}$-lb. flattened steel ball with a spherical striking surface, having a radius of $1\frac{1}{8}$ inches. The sample to be tested is placed loosely against a $\frac{5}{8}$-inch pine board and the pendulum is allowed to swing through an angle of about 30 degrees and strike the test-piece, the blows being repeated (with the pendulum moving through a greater angle at each blow) until the test-piece is broken. The impact strength is then calculated from one of the following formulæ :—

$$E=HW \text{ or } E=W(1-L\cos A)^{3}$$

where E is the energy of impact in foot-pounds, H is the height of drop in feet$=1-L\cos A$, where A=the angle through which the pendulum swings, and L=the length of the arm in feet. W is the weight of the hammer in pounds.

[1] *J. Amer. Cer. Soc., Year Book* 1921-1922.

[2] *J. Amer. Cer. Soc.*, **2**, 227 (1919).

[3] Where the angle of swing is greater than 90 degrees $H=L(1-\sin A)$.

E. Schramm [1] uses a similar device for testing the resistance of china ware to chipping, but employs a pendulum about 18 inches long consisting of a $\frac{3}{8}$-inch brass tube, the bob being a piece of $1\frac{1}{4}$-inch steel rod. The piece to be tested is arranged so that the pendulum strikes its edge.

Impact tests are also used for measuring the strength of floor tiles. The method recommended by F. B. O'Connor [2] consists in supporting the tile on two knife edges, the space between being filled level with plaster of Paris to correspond to the bedding of the tile. A hemisphere 2 inches diameter is attached to a sliding drop weighing 3 lbs. and is so placed that, when the drop falls, it strikes the tile exactly in the centre. The test is carried out by first allowing the weight to fall from a height of 1 inch and then increasing the height 1 inch at a time until fracture occurs. The test is not very accurate, but is sufficiently so for practical purposes. By this method, O'Connor found the height of drop which caused fracture varied from 1·8 inches to 10 inches, according to the nature of the tile.

Another important form of impact test is known as the " rattler " test (p. 200).

Torsion Tests.—The resistance of a clay paste or finished article to torsion is not usually of much importance, but may be determined by attaching one end of a test-piece of the material to a fixed support and twisting the other until fracture occurs, the resistance to torsion being expressed by the number of complete turns of the free end which must be made in order to break the test-piece. The latter should be in the form of a long rod or bar and the twisting should be effected slowly, or low results will be obtained.

Deformability Tests.—The deformability of ceramic materials may be determined by means of (*a*) a loaded rod or " plunger " such as a Vicat needle (fig. 14), and observing either the weight required to cause the " needle " to sink into the material to a prescribed depth in a prescribed time, or the time required for a needle of a given weight to make an impression of a given depth. The end of the Vicat needle, which makes the impression, is usually 1 mm. square and the " needle " weighs 300 grams. The needle may be graduated so that the depth of the impression may readily be measured. In clay pastes, it is usually allowed to make an impression 30 mm. deep. For fired articles and hard materials, a much heavier weight or, in some cases, hydraulic or other easily measurable pressure must be used to produce an impression.

(*b*) The weight or pressure required to reduce the height of a cylinder of the material to be tested by 1 inch (or other prescribed amount) in a given time.

In both these methods, the duration of the test is important, as a small weight acting through a long period may have a deforming power equal to that of a much greater pressure acting for a shorter time.

According to Ashley, the deformability of a sample may be found by dividing the air-shrinkage of the cast clay by the Jackson-Purdy surface-factor (p. 56), or by multiplying the colloid concentration by the specific air-shrinkage.

Rattler tests are chiefly used for testing bricks for use in roads in order to

[1] *J. Amer. Cer. Soc.*, **5**, 136 (1922).
[2] *Trans. Amer. Cer. Soc.*, **15**, 233 (1913).

determine (*a*) whether the bricks are tough enough to resist the forces of impact and abrasion to which they are subjected when in use, and (*b*) whether the material is uniform in quality. The toughness is determined by the average loss of weight which the pieces to be tested undergo as the result of chipping or breaking and the uniformity of the variation in the weight of the individual bricks or other articles after the completion of the test.

The standard method of conducting the rattler test for paving bricks adopted by the National Brick Manufacturers' Association of the U.S.A., and approved by various distinguished engineers, is as follows :—

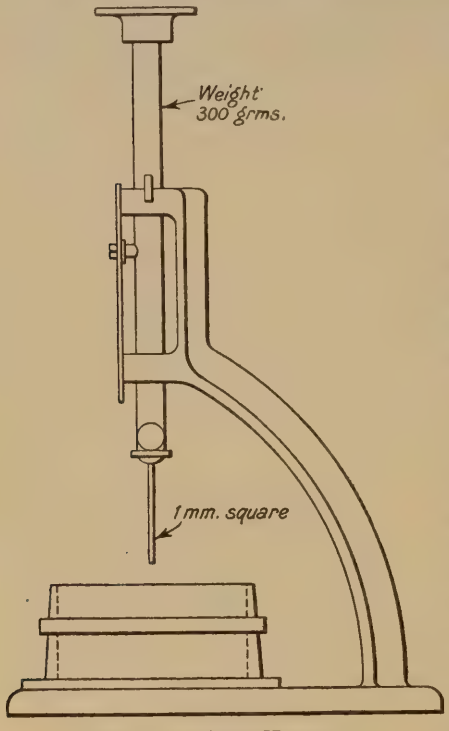


Fig. 14.—Vicat Needle.

The standard machine is 28 inches diameter and 20 inches in length, measured inside the chamber. Other machines may be used, varying in diameter between 26 inches and 30 inches, and in length from 18 inches to 24 inches, but if this is done a record of it must be attached to the official report. Long rattlers must be cut up into sections of suitable length by the insertion of an iron diaphragm at the proper point.

The barrel may be driven by trunnions at one or both ends, or by rollers underneath, but in no case should a shaft pass through the rattler chamber. The cross-section of the barrel should be a regular polygon, having fourteen sides. The heads should be composed of grey cast iron, not chilled nor case-hardened. The staves should preferably be composed of steel plates, as cast iron flakes, and ultimately breaks under the wearing action of the bucks. There should be a space of $\frac{1}{4}$ inch between the staves for the escape of the dust and small pieces. Other machines may be used having from twelve to sixteen staves, with openings from $\frac{1}{8}$ inch to $\frac{3}{8}$ inch between staves, but if this is done a record of it must be attached to the official report of the test.

All tests must be executed on charges containing but one make of material at a time. The charge should be composed of the bricks to be tested and iron abrasive material. The brick charge should consist of that number of whole bricks or blocks whose combined volume most nearly amounts to 1000 cubic inches or 8 per cent. of the cubic contents of the rattling chamber. (Nine, ten, or eleven are the number required for the ordinary sizes on the market.) The abrasive charge should consist of 300 lbs. of shot made of ordinary machinery cast iron. This shot should be of two sizes, as described below, and the shot charge should be composed of one-fourth (75 lbs.) of the larger size and three-fourths (225 lbs.) of the smaller size.

The larger size should weigh about $7\frac{1}{2}$ lbs. each and be $2\frac{1}{2}$ inches square and $4\frac{1}{2}$ inches long, with slightly rounded edges. The smaller size should be $1\frac{1}{2}$-inch cubes weighing about $\frac{7}{8}$ lbs. each, with square corners and edges. The individual shots should be replaced by new ones when they have lost one-tenth of their original weight.

The number of the revolutions of the standard test should be 1800 and the speed of rotation should not fall below 28 nor exceed 30 per minute. The belt-power should be sufficient to rotate the rattler at the same speed whether charged or empty.

The bricks composing a charge should be thoroughly dried and accurately weighed before making the test.

At the conclusion of the test, all the pieces should be removed from the barrel and those larger than 2 inches diameter—which, with good bricks, will consist of the slightly-chipped bricks—are then weighed and the loss in weight, as compared with that of the bricks prior to the test, is calculated as a percentage of the dry bricks composing the charge, and no result should be considered satisfactory unless it is the average of two distinct and complete tests, made on separate charges of brick.

As the machine just described was designed for American bricks—which are smaller than British ones—the author prefers a barrel 30 inches in diameter and 24 inches in length.

The amount of material lost (*i.e.* reduced to pieces less than 2 inches diameter) in a rattler test indicates roughly the durability of the material when in use, etc., whilst the respective loss of weight of the individual articles used in each test indicates the uniformity, or otherwise, of the quality. Thus a charge in which the loss on the individual bricks varied greatly would indicate lack of uniformity, and in specifying the resistance to the rattler test it is customary to state that the average loss on each charge should be not more than x per cent. and the maximum loss on any individual sample not more than y per cent.

Freezing Tests.—Some idea of the probable effect of exposure to frost may be gained by exposing the goods or materials to a "freezing test," such as is frequently applied to building materials. In one form of this test, the article or material to be tested is dried at 110° C., weighed, and boiled in water for thirty minutes. It is then allowed to cool and is placed in ice-cold water for one hour, after which it is placed in a refrigerator and kept at about −7° C. or 20° F. for twenty-four hours. It is then thawed and boiled again. This treatment is repeated twenty times, the loss in weight being noted each time and expressed as a percentage of the total dry weight of the article. It was at one time supposed that there is a relationship between the porosity of burned-clay goods and their resistance to freezing, but this is not the case.

A more rapid "freezing test" consists in immersing the article for forty-eight hours in a 15 per cent. solution of sodium sulphate in water at 21° C., withdrawing it, and then placing it in a dryer at 110° C. for about seven hours. This treatment is repeated as often as may be desired. H. F. Staley has stated that the effect of such treatment is equal to two ordinary freezing tests, the pressure of the crystals of sodium sulphate being similar in action to that of ice.

The freezing test of the American Society for Testing Materials consists in

saturating five bricks by placing them in cold water and then heating the water to a temperature of 200° F. in thirty minutes. The soaked samples are then placed in ice water for at least one hour, after which they are weighed and then frozen in a refrigerator with all surfaces exposed at a temperature of less than 15° F. for at least five hours. The samples are then removed and placed in water at a temperature of 150°–200° F. for one hour, the freezing and thawing being repeated twenty times. After this the bricks are re-weighed and the loss in weight, as well as any visible alterations, are noted.

In another form of freezing test, the bricks or other articles, after being frozen and thawed for a prescribed number of times, are dried, and their crushing strength is then determined and compared with that of the original bricks. The effects of the freezing are then expressed in terms of the percentage loss in crushing strength.

Binding-power Tests.—The binding power of a ceramic material may be regarded as (*a*) the force which unites its individual particles together, and this is estimated from the tensile, compression or cross-breaking strengths (pp. 193-197); (*b*) the power possessed by a clay or other " bond " to unite particles of other material and so form a coherent mass. The determination of binding power is described in Chapter VI.

CHAPTER V

THE SPECIFIC GRAVITY AND DENSITY OF CERAMIC MATERIALS

The terms *density* and *specific gravity* are often confused, so that care should be taken to understand their significance clearly.

The term *density* is often used in two different ways—(*a*) to signify the relation between the weight and volume of an article or material as a whole (including any pores or 'voids') and that of the weight of an equal volume of water, and (*b*) to indicate the relation between the weight and volume of the individual grains of material as compared with that of an equal volume of water, *i.e.*, the true specific gravity. The latter use of the term should be avoided and for the former it is better to use the term *apparent density*, as this clearly separates it from the *specific gravity*. A still better, though somewhat cumbersome, term for apparent density is *volume-weight*, which describes exactly what it is intended to represent without any risk of confusion. The term "volume-weight" is usually confined to relatively large quantities and is commonly expressed in "lbs. per cubic foot," "grammes per litre," or "ounces per pint."

The "*true*" *specific gravity* of a substance is the relation between its weight and that of an equal volume of water. If applied to a porous material, this term should be strictly confined to the specific gravity of the material after it has been reduced to a fine powder, *i.e.* to the specific gravity of the individual grains of which the material is composed.

The term *apparent specific gravity* or *bulk specific gravity* is used to indicate the relation between the weight of a mass of material as a whole and that of a volume of water equal to the total volume of the mass less the volume which can be filled with water (*i.e.* the volume of the solid material plus the sealed pores). Thus, a piece of burned clay may have an *apparent specific gravity* of 2·46, an *apparent density* of 1·965, corresponding to a *volume weight* of 1965 grams per litre or 122 lbs. per cubic foot, whilst its *true specific gravity* is 2·62. Such a specimen might consist of 75 c.c. of solid material, 5 c.c. of sealed pores, and 20 c.c. of open pores, the total weight being 196·5 grams and the total volume 100 c.c. From these figures the true specific gravity is found by dividing the weight of the mass (that of the air being neglected) by the volume of solid matter, namely, $\frac{196{\cdot}5}{75}=2{\cdot}62$, whilst the apparent specific gravity

is found by dividing the weight of the mass by the volume of solid matter plus that of the sealed pores, namely $\frac{196{\cdot}5}{100}=1{\cdot}965$, as stated above.

Many ceramic materials—especially when fired—contain "sealed pores" into which water cannot penetrate. These reduce the apparent specific gravity of the material, so that the true specific gravity cannot always be found by subtracting the volume of the pores (as ascertained from the volume of water absorbed by the material) from the total volume of the mass, for the result so obtained is not necessarily the volume of the solid matter, but the volume of the solid matter plus that of the sealed pores. When a material is ground to a fine powder, however, the sealed pores are destroyed and the sum of the volume of the individual grains forming the powder is the true volume of the solid matter, and from this the *true specific gravity* is obtained. The difference between the true and apparent specific gravities is thus found to depend on the nature of the material examined.

The study of the apparent density and specific gravity of ceramic materials is of great importance as a means of determining the quality of the raw materials and of the finished products, and also in estimating the efficiency of the mode of manufacture. Thus, the study of the true specific gravity of the raw materials used in the manufacture of silica and magnesia bricks and of the fired products, provides a means of estimating the completeness or otherwise of the treatment in the kiln and of the temperature to which a given material requires to be heated.

A study of the apparent density and specific gravity of clays is also of great value in ascertaining the maximum temperature to which they can safely be heated and sometimes may be used to determine the effectiveness of the firing. As the specific gravity of a material depends upon its weight and volume, this property is possessed by all substances no matter in which state they occur.[1] Hence, it is possible to determine the specific gravity of a gas, a liquid, or a solid. The specific gravity of gases is of minor interest in connection with ceramic materials, but a knowledge of the specific gravity of the liquids known as "slips" and used in the application of glazes and engobes, is very important in order to secure uniform results. For instance, if a glazing slip has too low a specific gravity, that is, if it is "too thin," an insufficient coating of glaze may be applied to the ware, whilst if the specific gravity is too great, that is, if the slip is "too thick," the coating may be uneven and may cause various troubles and defects.

Changes in the specific gravity of the solid substances used in making slips may also affect the specific gravity of the latter. Thus, the effect of calcination on the specific gravity of flint may cause the weight of flint in a slip weighing 32 oz. per pint to vary as much as 13 per cent. on account of the specific gravity of the calcined flint varying between 2·6 and 2·2. The potter who is unaware of this, and who is content to make his flint slip to a constant volume weight of 32 ozs. per pint, may find that variations in the specific gravity of the solid flint may make all the difference between a satisfactory and a badly-crazed body.

[1] The specific gravities and specific volumes of colloidal sols do not follow the ordinary rule for mixtures.

It will thus be seen that the specific gravity of ceramic materials—both when raw and during various stages of manufacture—is of great importance.

Factors which influence Apparent Density

The apparent density and volume-weight of a substance are affected by, and to some extent are dependent upon—

(*a*) The texture of the material if a solid and particularly if it is porous.

(*b*) The true specific gravity of the material.

(*c*) The proportion of sealed pores present.

(*d*) The temperature of the material.

(*e*) The mode of preparation and manufacture in so far as these affect the foregoing properties.

Texture and Porosity.—As the apparent density is the relation between the volume and weight of the mass as a whole, the smaller the space into which the solid matter can be packed the greater will be its apparent density, so that the shape and size of the grains and the grading of the mixture greatly influence this figure. If a material has a porous texture it will necessarily have a low apparent density, because a considerable portion of the volume of the mass will be occupied by the light-weighing air in the pores. On the other hand, a material of a glassy or vitrified nature will have its apparent density and true specific gravity represented by the same figure, because there are in it no pores to reduce the apparent density to below that of the true specific gravity.

The influence of these factors in producing compact and dense or light and porous materials is described in Chapter II.

The **true specific gravity** of the solid portion of the material will affect the apparent density, because the greater the true specific gravity the greater (other things being equal) will be the apparent density. Thus, a piece of carborundum having the same proportionate volume of pores as a piece of fireclay brick will have a greater apparent density because—whilst both pieces have the same total volume and the same volume of solid grains, the carborundum has a true specific gravity of 3·17–3·21, whilst the fireclay brick has a true specific gravity of only 2·6.

The **proportion of sealed pores**, *i.e.* those which are not filled by immersing the material in water, will affect the apparent density, because the true specific gravity of such pores is extremely low.

The **temperature** of a material affects its apparent density because most substances tend to expand or contract when heated, and this change in volume has a corresponding effect in reducing or increasing the apparent density. For this reason, determinations of the apparent density should be made at 15° C. or 60° F. or corrected to that temperature, or comparisons may be erroneous. Sometimes the effect of heat is complicated by the presence of two or more substances in a clay or other ceramic material. Thus, when clays are heated, the resulting shrinkage tends to increase the apparent density, but as the clay decomposes it changes its true specific gravity and tends to decrease it; any silica present will expand—if the temperature is

sufficiently high—and thus both its specific gravity and apparent density will be reduced. The final effect of all these changes will depend on their relative activity.

In silica bricks, the apparent density is decreased by the expansion of the silica when heated, and this involves a lowering of the specific gravity of the materials composing the mass (see p. 215).

The apparent density of china clay in the raw state is generally about 1·6 or 1·7. It decreases on heating as water is evaporated from the moist material and then increases as the empty spaces begin to disappear. As china clay does not readily vitrify, it does not show the marked decrease in apparent specific gravity noticeable when less pure clays are heated rapidly to about 970° C.

E. M. Firth, F. W. Hodkin, and W. E. S. Turner [1] found the apparent density of china clay to increase as follows :—

TABLE LXXXIII.—*Effect of Heat on Density of China Clay*

Temperature, ° C.	Apparent Density.	Temperature, ° C.	Apparent Density.
600	1·20	1200	1·77
750	1·19	1300	2·19
900	1·14	1400	2·36
1000	1·25	1500	2·44
1100	1·41		

The **mode of preparation and of manufacture** influence the apparent density in various ways, the most important of which are as follows :—

(*a*) The closeness with which the particles of material are packed has an important influence. For instance, hand-moulded articles usually have a lower apparent density than machine-made ones on account of the smaller amount of pressure employed and, consequently, the lesser compacting of the mass.

(*b*) The proportion of moisture present affects the apparent density, as water has a lower specific gravity than the solid ceramic materials, and when it separates the particles it increases the volume of the mass at a greater rate than it increases its weight.

The effect of the amount of moisture used in making firebricks is shown in Table LXXXIV, which shows some results obtained by Nesbitt and Bell.[2]

TABLE LXXXIV.—*Effect of Moisture on Apparent Density*

Moisture, per cent.	Apparent Density.	Moisture, per cent.	Apparent Density.
4	2·11	8·5	2·16
6	2·17	10	2·10
8	2·19	12	2·06

[1] *J. Soc. Glass Tech.*, **4**, 265 (1920).

[2] *Am. Soc. Test. Mat.*, 1917.

(*c*) The drying and firing affect the apparent density of a ceramic material because the individual grains tend to draw closer together and so occupy a small volume. Hence, the apparent density—especially of clays and plastic materials—at first increases owing to the shrinkage of the mass. When vitrification commences, however, the apparent density may begin to decrease on account of the formation of silicates of less density, and the decrease continues (if the heating is sufficiently intense) until the whole mass is fused. Long-continued heating at high temperatures reduces the apparent density of all natural silicates such as felspars, granites, porphyry, etc., partly on account of changes in the true specific gravity and the formation of other substances such as cristobalite and tridymite from quartz, and partly as a result of the formation of sealed pores. When many of the less pure clays are heated, a temperature is reached—depending on the nature of the clay—at which the apparent density decreases rapidly owing to the formation of bubbles of gas, many of which cannot escape and so cause the material to swell considerably. As such swollen material is generally useless, its formation usually marks the maximum temperature to which that particular clay can safely be heated; further heating (overheating) causes the formation of a vesicular structure, with resultant bloating, distortion, and spoiling of the material, as shown by a decrease of the apparent specific gravity. This is well indicated in Table LXXXV.

Factors influencing Apparent Specific Gravity

The apparent specific gravity is affected by (*a*) the true specific gravity of the solid matter present, and (*b*) the proportion of sealed pores.

The proportion of sealed pores usually increases on heating, because of chemical and physical reactions which take place. The extent of the increase is dependent on the nature of the material, the temperature and duration of heating, etc. Thus, many red-burning clays are very greatly affected by this action, whilst the apparent specific gravity of good silica bricks is scarcely altered.

Clays generally increase in apparent specific gravity on firing, but if they are over-heated a vesicular structure develops and the apparent specific gravity is lowered.

The difference between the true and apparent specific gravities of several clays at various temperatures is shown in Table LXXXV, compiled from figures obtained by Bleininger and Montgomery,[1] where A is the maximum burning temperature without the production of vesicular structure and B is the difference between the true specific gravity and the apparent specific gravity at that temperature. At the temperature in column C the clay is distinctly overfired and column D shows the difference between the true and apparent specific gravities at these temperatures, the increased difference being due to the production of a vesicular structure.

More refractory clays may be heated to a higher temperature without decreasing the apparent specific gravity, as shown in Table LXXXVI, due to Firth, Hodkin, and Turner.

[1] *Trans. Amer. Cer. Soc.*, **15**, 71 (1913).

TABLE LXXXV.—*Effect of Heat on Specific Gravity of Clay*

	A.	B.	C.	D.
	° C.		° C.	
Surface clay . . .	1070	0·100	1230	0·350
„ „ . . .	1030	0·200	1170	0·385
Shale	1030	0·110	1210	0·295
„	1030	0·140	1190	0·840
Fireclay . . .	1090	0·205	1250	0·175
„ . . .	1090	0·110	1250	0·240

TABLE LXXXVI.—*Effect of Heat on Apparent Specific Gravity of Fireclays*

	Fluxes, per cent.	600° C.	750° C.	900° C.	1000° C.	1100° C.	1200° C.	1300° C.	1400° C.	Total Increase.
Stourbridge fireclay .	2·62	1·71	1·73	1·73	1·79	1·92	2·02	2·06	1·90	0·19
Halifax . . .	2·42	1·73	1·71	1·72	1·77	1·82	1·91	2·03	2·20	0·47
Stourbridge . .	1·80	1·87	1·85	1·85	1·87	1·96	2·03	2·03	2·24	0·37
Grossalmerode . .	1·74	1·89	1·86	1·86	1·87	1·95	2·04	2·06	2·10	0·21
Kilwinning aluminous shale . . .	1·57	1·68	1·67	1·73	1·72	1·74	1·80	1·81	1·86	0·08
Ayrshire bauxitic clay	0·69	1·70	1·72	1·74	1·84	1·83	1·91	2·06	2·14	0·44

Office [1] found that the difference between the true and apparent specific gravities of silica bricks is about 0·011, the true specific gravity being rather higher than the apparent specific gravity.

FACTORS INFLUENCING THE TRUE SPECIFIC GRAVITY

The true specific gravity of ceramic materials is affected by various factors.

(*a*) The physical form of the material.

(*b*) The chemical constitution of the material, which is important when it is changed by heating.

(*c*) The impurities (if any) in the material.

(*d*) The temperature of the material.

(*e*) The temperature to which the material has previously been heated and the duration of the heating (if any).

(*f*) The rate (if any) at which the material has been cooled.

The **physical form** of the material greatly influences its specific gravity, a substance in the amorphous or gel state having a much lower specific gravity than when in the crystalline state. The true specific gravity of a crystal is usually reduced when

[1] *J. Amer. Cer. Soc.*, **2**, 833 (1919).

it is converted into the molten or liquid state, and much lower if it is in the gaseous or vaporous state. Water is an interesting exception, as in the solid state (*ice*) it has a specific gravity of 0·9175, in the liquid state a specific gravity of 1·000, and in the gaseous state (steam) a specific gravity of 0·00077 (see also p. 211).

Some forms of silica attain the minimum specific gravity much more readily than others, flint being transformed much more readily than quartz, so that, in order to avoid an unnecessary expenditure of fuel in making silica bricks it is desirable that the materials used should be such as will attain the minimum specific gravity as quickly as possible. Any changes which do not take place during manufacture may continue when the bricks, etc., are in use, and may then cause damage and loss. The texture of a ceramic material influences the true specific gravity, inasmuch as when a fine-grained material is heated any change in the specific gravity can occur more rapidly than in the same material composed of coarser grains, as the latter are not in such intimate contact with the various fluxes and require longer for the heat to penetrate through them and thus induce the change.

For further particulars respecting the influence of the physical form on the true specific gravity, see p. 210.

The **chemical constitution** influences the true specific gravity of a material because the rearrangement of its constituent atoms must usually affect the space which they occupy. Thus, when quartz is converted into cristobalite or tridymite it probably undergoes an atomic rearrangement, which results in a mass of different unit volume being formed, with the result that the true specific gravity is changed from 2·65 to 2·28 in the case of tridymite and 2·34 in the case of cristobalite. The precise nature of the change is not known ; it may be due to differences in the number of atoms in each molecule of the various forms of silica. Thus, as tridymite and cristobalite each have a lower specific gravity than quartz, they may have fewer atoms in their respective molecules. Analogous changes are well known in organic chemistry, but are extremely difficult to investigate in the case of silica.

The effect of **impurities** on the specific gravity of a material is twofold ; they affect it directly like any other admixture, but they also affect it by reacting with the material, altering its physical form and chemical constitution when the conditions are favourable (see later).

The **temperature** of the material affects its specific gravity for the same reason as it affects its apparent density (see p. 205).

The **previously attained temperature** and **duration of heating** of the material affect the true specific gravity as a result of the physical and chemical changes which occur. This must be considered in conjunction with the duration of heating, as a long period of heating at a lower temperature is often equivalent to a short period of heating at a higher temperature. The specific gravity of clayey materials is reduced roughly in proportion to the temperature attained and the duration of heating in conjunction with other factors previously mentioned, the change being accelerated by an increase in either the temperature or the duration of the heating. Thus, clays are decomposed, and the resultant substances have different specific gravities from those of the original material. Similarly, quartz on heating is converted into

tridymite and cristobalite, each of which has a different specific gravity from quartz; whilst magnesia, when heated sufficiently, changes into different allotropic forms in the same way as silica.

When a complex or impure ceramic material is heated, the impurities present may play an important part in changing its true specific gravity by combining with a portion of it to form a fusible material of a different nature and specific gravity from that of the original substance. For example, clays from various sources differ in specific gravity on account of variations in their composition and structure. On heating, these variations cause the clays to act in different ways. The Table on p. 213 shows that whilst ordinary fireclays and most red-burning clays decrease in true specific gravity on firing, some highly-aluminous clays increase in specific gravity. The true specific gravity of china clay and kaolin—when these substances are heated to 1500° C.—first increases from about 2·4 to 2·6, and then decreases, the final result being a slight increase. In the case of less pure clays, or on the addition of fluxes, the specific gravity of the material, when heated to a sufficient temperature to combine to form fresh compounds, is usually reduced, as the products generally possess a smaller specific gravity. Thus, Bleininger and Moore [1] found that the true specific gravity of clays containing felspar or Cornish stone was reduced when the latter began to fuse, the speed of decrease depending on the rate of solution of the clay by the flux. Hence, ball clays—which contain a large proportion of flux—are dissolved more rapidly than kaolins. The addition of lime to a clay causes a rapid decrease in the specific gravity of the clay when the mixture is heated to about 1100° C.

E. M. Firth and W. E. S. Turner [2] have found that the true specific gravity of aluminous fireclays to which felspar is added is less than that of ordinary clay burned at the same temperature. The addition of 9 per cent. of felspar to an Ayrshire aluminous fireclay decreased the specific gravity of the material (after it had been fired at 1500° C.) from 2·86 to 2·67, whilst the addition of 18·1 per cent. of felspar decreased its specific gravity to 2·53. The addition of 9·7 per cent. of felspar to a Kilwinning fireclay reduced the specific gravity from 2·69 to 2·57, and 19·4 per cent. of felspar reduced it to 2·41.

In the case of silica bricks, the true specific gravity is reduced by the presence of fluxes, which aid the transformation of the silica from quartz to one or other of the low specific gravity forms of silica. An increase in the percentage of flux increases the rate of conversion and decreases the true specific gravity, whilst an increase in the number of individual fluxes present increases the rate of conversion and decreases the specific gravity of the material. Scott [3] found that the addition of simple oxides as bonds to silica bricks reduced the specific gravity up to about Cone 14 (1410° C.), but at higher temperatures little change took place. With mixed oxides, however, a gradual reduction in the specific gravity took place independently of the temperature.

[1] *Trans. Amer. Cer. Soc.*, **10**, 293 (1908).
[2] *J. Soc. Glass Tech.*, **4**, 393 (1920).
[3] *Trans. Eng. Cer. Soc.*, **18**, 486 (1918–19).

The true specific gravity of magnesites containing iron oxide increases when they are heated, more rapidly than that of the purer ones, on account of the iron oxide aiding the transformation of the magnesite into periclase.

The greatest change effected by heat in the specific gravity of a material is that which occurs when the material melts or fuses completely. Even when only partial fusion occurs the changes in the specific gravity are often much more rapid than at a slightly lower temperature, and the product may be quite different in character, even though its composition (as shown by analysis) is unchanged. Thus, if crystalline quartz is heated to any temperature below its fusing-point its specific gravity cannot be reduced below about 2·3, and that of other siliceous materials of a crystalline nature cannot be reduced below 2·32 or 2·33 even by prolonged heating in an open-hearth furnace, provided partial fusion does not occur, yet as soon as sufficient fused material is formed the specific gravity drops rapidly to 2·2. This change in behaviour is due to the transformation, during fusion, from crystalline to the amorphous state; the explanation is confirmed by the fact that flint and other amorphous forms of silica may attain a specific gravity as low as 2·2 before fusing, and no sudden change occurs in their specific gravity when the mass melts. The change in specific gravity which occurs on melting various siliceous materials is shown in Table LXXXVII, due to Purdy and Moore.[1]

TABLE LXXXVII.—*Effect of Melting on Specific Gravity*

Material.	Specific Gravity in Crystalline Form.	Specific Gravity in Glassy Form.	Reduction in Specific Gravity, per cent.
Quartz	2·6630	2·2800	16·3
,,	2·6500	2·1900	17·3
Mica	3·0719	2·2405	27·0
Orthoclase	2·5740	2·3280	9·6
,,	2·5883	2·3073	10·9
Microcline	2·5393	2·3069	9·1
Allite	2·6040	2·0410	21·6
Oligoclase	2·6600	2·2580	15·1
,,	2·6061	2·3621	9·1
,,	2·6141	2·1765	16·7
Labradorite	2·7333	2·5673	6·1

The **rate of cooling** often has an important effect on the specific gravity of a material, especially where the changes in specific gravity due to heating are reversible

[1] *Am. Cer. Soc.*, 9, 226 (1907).

on cooling. Thus, in the case of silica, if the cooling is sufficiently slow the low specific gravity forms revert to the high-specific gravity form, viz. quartz, but if the cooling is very rapid these changes are unable to take place and the low specific gravity form of the hot material is retained.

The Apparent Density and True Specific Gravity of various Ceramic Materials

It is often very important to know both the apparent density and the specific gravity of various raw materials used in the ceramic industries, as this knowledge gives some indication as to the probable behaviour of the materials when in use. The specific gravity of the finished or partially-finished products often serves a similar purpose, and also enables the manufacturer or user to decide whether the treatment during manufacture has been sufficient and whether the products are suitable for a particular purpose.

Clays and Clay Products.—The volume-weight or apparent density of raw clays varies according to their compactness or otherwise, the harder rock clays being the densest. According to J. L. Crawford,[1] the apparent density of various clays is as follows :—

Plastic fireclay . . .	1·52–1·53
Brick clay . . .	2·0
Flint clay . . .	1·85–1·86
Washed pot clay . .	1·87–1·88

but such large variations occur in clays from different localities that no general figures can be truly representative.

The true specific gravity of raw clay is usually between 2·5 and 2·8 ; it varies according to the chemical composition of the material. The specific gravity of fireclay is usually between 2·6 and 2·75, according to the extent to which the clay has been indurated.

As explained on p. 205, the apparent density of ceramic materials changes considerably during the various stages of manufacture, and especially in drying, mixing, and burning, but the true specific gravity is not affected to so great an extent unless a large amount of vitrification occurs or the burning is badly controlled.

Clays when heated increase slightly in specific gravity up to the temperature required to drive off the combined water, but when all the water is removed the specific gravity is reduced. When china clay with a specific gravity of 2·4 is heated to the temperature of decomposition, its specific gravity increases up to nearly 2·7 and then falls again to about 2·5.

J. M. Knote [2] found that when any clay is decomposed by heat the resultant material has a lower specific gravity than the raw clay, but when heated to a higher

[1] *J. Amer. Cer. Soc.*, **5**, 394 (1922).
[2] *Trans. Amer. Cer. Soc.*, **12**, 226 (1910).

temperature the specific gravity again increases. He also found a sudden increase in specific gravity at about 950° C., at which temperature Le Chatelier found an exothermic reaction occurs. Knote suggests that the low specific gravity at the decomposition point is due to the formation of substances of lower specific gravity than raw clay, and that the increase in specific gravity above this temperature may possibly be due to further loss of water. The sudden increase in specific gravity at 950° C., he suggests, may be due to the formation of sillimanite, $Al_2O_3 2SiO_2$, but this has not been proved.

J. M. Knote has also found that some feebly plastic clays (such as flint clays) have a rather higher specific gravity after being heated to 900° C. than plastic ones, and suggests that this is due to differences in the physical condition of the two kinds of clay. Table LXXXVIII, due to Firth, Hodkin, and Turner, shows the effect of heating on the specific gravity of different types of clays (chiefly fireclays).

TABLE LXXXVIII.—*Specific Gravity of Burned Clays*

	Flux, per cent.	600° C.	750° C.	900° C.	1000° C.	1100° C.	1200°C.	1300°C.	1400° C.	Change.
Ruabon aluminous fire-clay	4·24	2·55	2·57	2·56	2·59	2·58	2·52	2·49	2·37	−0·18
Kilwinning	3·05	2·46	2·52	2·55	2·66	2·55	2·56	2·55	2·50	+0·04
Mansfield	2·58	2·45	2·53	2·61	2·65	2·65	2·63	2·53	2·50	+0·05
Stourbridge	2·02	2·50	..	2·60	2·64	2·57	2·57	2·63	2·62	+0·12
Kilwinning aluminous shale	1·57	2·53	2·63	2·74	2·72	2·70	2·71	2·72	2·72	+0·19
Halifax	1·14	2·50	2·54	2·50	2·53	2·54	2·57	2·61	2·54	+0·04
Ayrshire bauxitic shale	0·69	2·57	2·64	2·67	2·82	2·75	2·79	2·88	2·88	+0·31
Stourbridge	2·62	2·48	2·51	2·60	2·62	2·52	2·50	2·46	2·33	−0·15
,,	1·80	2·50	2·52	2·55	2·60	2·56	2·51	2·49	2·38	−0·12
Halifax	2·42	2·47	2·48	2·37	2·41	2·43	2·48	2·45	2·34	−0·13
Grossalmerode	1·74	2·51	2·64	2·63	2·61	2·60	2·56	2·53	2·41	−0·10

It will be seen that, in the last four clays in the Table, the specific gravity decreases most in the ones containing the largest proportion of flux. In the first seven clays, however, the presence of a large amount of alumina causes variations and, in all cases but one, an increase in the specific gravity. The continued decrease in the specific gravity of overburned clays shows that molecular changes are still going on and that equilibrium is not reached at any convenient stage of vitrification.

Bleininger has stated that the more rapid the fall in the specific gravity during the heating of a clay, the more rapid will be the rate of vitrification and the shorter the vitrification-range. The rate at which the specific gravity changes thus indicates, to some extent, the value of a clay for any particular purpose, and is a valuable guide in the examination of fresh deposits of clay.

The apparent density of various burned argillaceous materials is shown in Table LXXXIX.

Ordinary brickwork, including mortar, usually has an apparent density of 1·5–1·7.

TABLE LXXXIX.—*Apparent Density of Various Clay Goods*

	Apparent Density.		Apparent Density.
Staffordshire red bricks .	1·87	Firebricks . . .	1·9–2·0
,, blue bricks	1·9	Very porous firebricks .	1·0 or more
,, brindled bricks .	1·9	Semi-grog bricks . .	1·83
Shale bricks . . .	1·81	Grog bricks . . .	1·8
Paving bricks . .	2·3 or more	Semi-porcelain . .	1·9–2·2
Tiles	1·4–2·0	Hard porcelain . .	2·15–2·45
		China ware . . .	2·25–2·4

The true specific gravity of burned clay is usually about 2·6, and is not greatly affected by the nature of the clay of which the goods are made unless some material other than water is added. Thus, if any silica is added in the course of manufacture, the specific gravity will be rather less. P. Goerens and S. W. Gilles [1] give the true specific gravity of various kinds of bricks as follows :—

TABLE XC.—*True Specific Gravity of Clay Wares*

Material.	True Specific Gravity.	Material.	True Specific Gravity.
Semi-grog bricks .	2·59	Shale bricks .	2·62
Grog bricks .	2·53	Lias ,, . .	2·80

The true specific gravity of *porcelain* varies from 2·24–2·35. The more complete the vitrification the lower will be the specific gravity, the decrease being continued as the material becomes increasingly viscous and finally fuses.

The effect of the composition of porcelain on its specific gravity is very marked. Usually, according to Potts and Knollman,[2] the true specific gravity increases somewhat on heating up to Cone 4 (1160° C.) and then decreases again, the specific gravity at Cone 8 (1250° C.) being less than at Cone 2 (1120° C.). In some porcelains, which contain a large proportion of flint, the true specific gravity gradually decreases on heating, on account of the conversion of the free silica to tridymite and cristobalite.

[1] *Mitteilungen aus dem eisenhüttentechnischen Int. der Königl. Techn. Hochschule, Aachen*, **7**, 1–15 (1916).

[2] *Trans. Amer. Cer. Soc.*, **15**, 283 (1913).

At Cone 8 (1250° C.) some porcelains which are rich in clay and low in felspar have a slightly higher true specific gravity than at Cone 4 (1160° C.), but most porcelains have a lower specific gravity after being heated, and it continues to diminish up to a temperature of Cone 12 (1350° C.). Some porcelains which are very rich in clay, however, remain almost unchanged.

Potts and Knollman also found that below Cone 8 an increase in the proportion of felspar in a porcelain increases the apparent specific gravity, but above Cone 8 (1250° C.) and up to Cone 12 (1350° C.) felspar facilitates the production of a vesicular or honeycomb structure, this being most pronounced in porcelains containing a large proportion of flint. The true specific gravity at Cone 2 (1120° C.) is decreased by increases in the proportion of felspar, the decrease commencing earlier with porcelains rich in flint, but is spread over a longer period. In porcelains rich in clay, the specific gravity begins to decrease a little later, but it then proceeds more rapidly.

Only a comparatively small amount of work has been done with regard to fixing standards for the volume-weight and specific gravities of different articles made of clay, but the work in this direction is now increasing. H. Burchartz [1] has suggested the following volume-weights and specific gravities for various (German) building materials :—

TABLE XCI.—*Specific Gravity and Volume-Weight of Building Bricks*

	Volume-Weight.	True Specific Gravity.
Clinker bricks	1·85	2·6–2·7
Hard-burned ware . . .	1·75	2·6–2·7
First-class building bricks . .	1·60	2·6–2·75

He suggests that no building bricks should have a true specific gravity of less than 2·50. The apparent density of a number of paving bricks should average not less than 2·35, and no single brick in the series should have an apparent density of less than 2·30.

Siliceous Materials.—The true specific gravities of various forms of silica used in the manufacture of siliceous refractory materials is shown in Table XCII.

The best materials for the production of highly siliceous refractory materials—as far as volume-changes are concerned—will be those having the lowest specific gravity or those in which the specific gravity is reduced most rapidly on heating. The volume-changes are not, however, the only matters to be considered, so that, in some cases, a material with a satisfactory volume-change cannot be used on account of some harmful property which it possesses. Thus, calcined flint, on account of the roundness of its grains, produces a weak mass, though otherwise it is quite satisfactory.

[1] *Mitt. Königl. Materialprüfungsamt*, **34**, 79 (1916).

TABLE XCII.—*Specific Gravity of Siliceous Materials*

Material.	Specific Gravity.	Material.	Specific Gravity.
Quartzite and crystalline quartz	2·59–2·66	Chalk flint	2·61
Close-grained quartzites	2·64–2·65	Calcined chalk flint	2·22
Open-grained ,,	2·60–2·62	Potters flint	2·3–2·4
Rock crystal	2·653	Kieselguhr	2·6
Chalcedony	2·55–2·61	Fused kieselguhr	2·22–2·35
Calcined chalcedony	2·2	Silica glass	2·194–2·213
Flint	2·61–2·63	Fused silica rocks	2·22

Table XCIII shows the specific gravity of various forms of silica such as occur when any form of silica is heated.

TABLE XCIII.—*Specific Gravity of Different Forms of Silica*

Form of Silica.	Specific Gravity.	Authority.
α-quartz	2·65	
β-quartz	2·633	
α-cristobalite	2·33	Endell.
	2·333	Fenner (artificial cristobalite).
	2·34	Mallard (natural cristobalite).
β-cristobalite	2·21	
α-tridymite	2·32	Endell.
	2·27	Fenner (artificial tridymite).
	2·28	Mallard (natural tridymite).
β-tridymite	2·32	
Quartz glass	2·21	Dana, Endell.
	2·194	Schwartz.

These products do not occur alone in any refractory material, but a well-fired article usually contains two or more of them in various proportions, which depend on the manner in which it has been heated. In such a mixture, the respective proportions of each, together with various other factors mentioned on pp. 205–212, determine the apparent density and specific gravity of the mass.

It has previously been shown (pp. 209–211) that the temperature attained, and more especially the duration of heating, is of great importance in the conversion of quartz to the low specific gravity forms of silica. Table XCVI (p. 218) shows the effect of heating various siliceous materials to a temperature of about 1430° C.

Similarly, Table XCIV, due to Howe and Kerr,[1] shows the effect of the temperature of burning on the specific gravity of silica bricks made from Medina quartzite.

TABLE XCIV.—*Effect of Burning Temperature on Specific Gravity of Silica Bricks*

Temperature. Cone.	True Specific Gravity.	Temperature. Cone.	True Specific Gravity.
11	2·50	17	2·33
14–15	2·38	18	2·31
16–17	2·35	19	2·30

Table XCV, due to Mellor and Campbell,[2] shows the effect of several heatings on the specific gravity of flint and quartz, the materials being heated to a temperature of 1300° C., allowed to cool, and then reheated ; this procedure was repeated as often as stated in the Table.

TABLE XCV.—*Specific Gravity Changes in Flint and Quartz*

No. of Firings.	Flint, Specific Gravity.	Quartz, Specific Gravity.	No. of Firings.	Flint, Specific Gravity.	Quartz, Specific Gravity.
0	2·61	2·66	8	2·22	2·35
1	2·34	2·58	9	2·22	2·34
2	2·26	2·50	10	2·22	2·33
3	2·23	2·45	11	2·22	2·32
4	2·23	2·42	12	2·22	2·32
5	2·23	2·39	13	2·22	2·32
6	2·23	2·38	14	2·22	2·32
7	2·23	2·36	15	2·22	2·32

Table XCVI, due to Rieke and Endell,[3] shows the changes in specific gravity

[1] *J. Amer. Cer. Soc.*, **5**, 166 (1922).
[2] *Trans. Eng. Cer. Soc.*, **14**, 80 (1915–16).
[3] *Silikat Zeitschrift*, 1913, No. 2.

occurring when various kinds of silica are repeatedly heated to a high temperature in a hard porcelain oven.

TABLE XCVI.—*Effect of Repeated Heating on Specific Gravity of Siliceous Materials*

Material.	Specific Gravity. Number of Times Heated in Oven.											
	Raw.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Quartz from Norwegian pegmatite (in pieces)	2·65	2·38	2·33	2·325	2·33	2·32	2·31	2·32	2·33	..	..	..
Quartz from Norwegian pegmatite (in powder)	2·65	2·37	2·34	2·34	2·335	2·33	..	..	..	..	..	..
Quartz sand from Hohenbocke	2·651	2·591	2·502	2·456	2·450	2·442	2·428	2·386	2·369	2·343	2·338	2·328
Pure Geyserite from Taurus	2·651	2·555	2·492	2·478	2·391	2·394	2·366	2·344	2·321	2·316	2·313	..
Average geyserite (ground)	2·651	2·456	2·361	2·349	2·333	2·317	2·306	2·307	..	..	..	..
Quartz crystal (St Gothard) (in pieces)	2·65	..	..	..	..	2·64	..	..	..	..	2·63	..
Quartz crystal (St Gothard) (in powder)	2·65	2·568	2·553	2·547	2·519	2·475	..	..	..	..	..	..
Flint (in pieces)	2·632	2·231	2·241	2·248	2·239	2·233	2·255	2·251	2·231	2·230	..	..
Chalcedony (in pieces)	2·607	2·16	2·17	2·17	2·19	..	..	..	..	..	..	..
Hydrated silica (Kahlbaum)	..	2·322	2·319	2·312	2·316	2·317	..	..	..	..	..	..
Quartz glass (Heræus)	2·21	2·327	2·328	2·33	..	..	..	..	..	..	..	..

Hohenbocke sand requires eleven heatings before its specific gravity is reduced to 2·33. Dinas rock requires to be heated for at least twenty hours at 1500°–1800° C. to reduce its specific gravity by the same amount. Carboniferous sandstones attain a minimum specific gravity more rapidly than do felsitic quartzose rocks, but not so rapidly as amorphous silica. According to O. Rebuffat,[1] the Italian Lago Negro quartzite has a specific gravity of 2·65 in the raw state, and on burning for only eight hours at 1300°–1350° C. the specific gravity is reduced to 2·25. He suggests that this is due to the presence of 0·31 per cent. of phosphoric anhydride, which facilitates the conversion of the silica into tridymite.

The apparent density of silica bricks is not quite so high as that of fireclay bricks; it varies according to the nature of the raw materials and the method of manufacture, but is usually between 1·5 and 1·88, the average being about 1·67. M'Dowell found the mixtures used in the United States for ordinary silica bricks to have a volume-weight between 1·637 and 1·678, that for silica shapes between 1·723 and 1·839, and a specially fine grade of silica blocks, 1·725 and 1·774.

The true specific gravity of silica bricks is generally between 2·3 and 2·6. K. H. Endell [2] gives the following figures for the specific gravity of silica bricks of various kinds :—

[1] *Trans. Eng. Cer. Soc.*, **21**, 66 (1921–22).
[2] *J. Amer. Cer. Soc.*, **5**, 209 (1922).

TABLE XCVII.—*Specific Gravity of Silica Bricks*

Type of Brick.	True Specific Gravity.
German open-hearth furnace brick .	2·37–2·50
,, coke oven brick . .	2·46–2·49
,, glass furnace brick . .	2·47
U.S.A. Medina quartzite brick .	2·34
,, Baraboo quartzite brick .	2·33
English ganister brick . . .	2·40
Swedish quartzite brick. . .	2·34–2·39

The American Ceramic Society specifies a specific gravity not exceeding 2·38 for silica bricks made from Medina quartzite and 2·42 for bricks made from Baraboo quartzite.

Phillipon [1] has found that silica bricks made with 60 per cent. of flour have a specific gravity of 2·33, whilst those with only 30 per cent. of silica flour have a specific gravity of 2·43.

Silica bricks made from flint or other form of amorphous silica should have a specific gravity of about 2·22–2·25.

The true specific gravity of burned silica bricks is of great importance ; it affords the best means of determining the effectiveness of the firing process. When the whole of the quartz has been transformed into one or other of the low specific gravity forms of silica (cristobalite and tridymite), the true specific gravity of the product is about 2·3. So low a specific gravity is never attained in practice, but quartzitic materials and silica bricks, etc., having a specific gravity of 2·40 or less are considered to be satisfactory. The incompleteness of the conversion is due to the slow rate at which it occurs at the temperatures attainable in commercial kilns.

The apparent density and specific gravity of various porous siliceous materials has been found by Sargent and Lundy [2] to be as follows :—

TABLE XCVIII.—*Density and Specific Gravity of Porous Siliceous Goods*

	Apparent Density.	True Specific Gravity.
Osceola . . .	2·06	2·55
Sigur . . .	0·79	1·78
Sil-o-cel . . .	0·478	2·29
Diddier . . .	0·459	1·42
Magnesia . . .	0·253	1·47
Nonpareil bricks .	0·467	0·84

[1] *Rev. de Métal.*, **15**, 487 (1918).

[2] *Power*, **95**, 593 (1917).

The apparent density of moler bricks varies, according to J. W. Richards,[1] from 0·87 to 1·13.

Kieselguhr, when heated between 700° and 1000° C., increases in apparent density. Kieselguhr which has been heated below 700° C. has an apparent density between 0·5 and 0·7, but when the material has been heated above 700° C. the apparent density increases rapidly until between 1100° and 1400° C. it is 1·4, and between 1400° and 1600° C. it is about 2·2. Between these temperatures—according to its purity—the material fuses, the apparent density last recorded being that of the fused material.

The specific gravity of transparent *silica glass* or "*fused quartz*" is about 2·2. The translucent variety known as vitreosil has a specific gravity of 2·08.

According to R. J. Montgomery,[2] the apparent density of *silica cement* varies from 2·40–2·45 at Cone 1 (1100° C.) to 2·20–2·38 at Cone 20 (1530° C.).

Asbestos varies in specific gravity according to the variety; chrysotile has a specific gravity of about 2·5, tremolite about 3·0, crocidolite about 3·2, and anthophyllite about 3·1.

Magnesia Refractory Materials.—The true specific gravity of various materials used in the manufacture of magnesia bricks, etc., is as follows :—

Magnesite spar, 2·9–3·1.

Crypto-crystalline magnesite, 2·85–2·95.

Breunnerite, 3·01–3·45.

Hydromagnesite, 2·1.

On heating magnesite, the specific gravity changes considerably. The lightly calcined material consists chiefly of a material termed *a-magnesia* by Mellor and has a specific gravity of 3·2. The intensely heated and fully shrunk material consists of periclase with a specific gravity of 3·674. Most commercial samples of calcined magnesite have a specific gravity between 2·85 and 3·65, according to the extent to which they have been burned.

Ditte gives the following figures for the specific gravity of magnesia which has been heated to different temperatures :—

Burned at 350° C.	. . . .	Specific gravity at 0° C., 3·1932
,, dull red heat	. . .	,, ,, ,, 3·2482
,, white heat	. . .	,, ,, ,, 3·5699

Moissan has published the following results of magnesia which has been more intensely heated :—

Heated in blast furnace (6 hours)	.	Specific gravity at 20° C., 3·577
,, in electric furnace (2 hours)	.	,, ,, ,, 3·587
,, to complete fusion	. .	,, ,, ,, 3·654

Magnesia which has a specific gravity of 3·2 or less can only be used for furnaces, etc., working at comparatively low temperatures. For those working at very high

[1] *Elect. and Metall. Ind.*, 7, 474.

[2] *Amer. Soc. for Testing Mils.* (1918).

temperatures a more perfectly burned product, consisting more largely of periclase, must be employed.

The specific gravity of magnesia bricks varies from 3·05 to 3·58. The particular figure is dependent upon the temperature at which the raw material was calcined and the duration of heating, the temperature at which the bricks were burned, and the duration of heating and the nature of the raw material used. It is very useful to know the volume-weight of the soft mixture used for making magnesia bricks, so that a uniform quantity of material may be sent to the press. At this stage of the manufacture the volume-weight indicates, to some extent, the shrinkage which will occur during the drying and burning, and the mixing should be arranged so as to give a material having such a volume-weight as will produce bricks of the required size.

Dolomite Materials.—Raw dolomite has a specific gravity of 2·85 and, when burned, it produces bricks with a true specific gravity of about 3·0.

Aluminous Materials (other than Clays).—Pure crystalline alumina has a specific gravity of 3·92, that of the alundum prepared by the Norton Company being 3·91. Raw bauxite usually has a specific gravity of about 2·9, and the bricks made from it of 3·2–3·8 according as the bauxite has been highly calcined or fused and recrystallised.

Zirconia.—The specific gravity of raw zirconia is 4·4–6·0 ; that of fully shrunk zirconia is 4·8–5·0. Zircon has a specific gravity of 4·2–4·86.

Graphite, when natural, has a specific gravity of 2·01–2·58, but when made by artificial means it is generally about 2·02. When compressed, the specific gravity of graphite may be increased considerably, that of very dense samples being a little short of 3·0. The specific gravity of carbon electrodes is usually between 1·88 and 1·98 ; their apparent density varies from 1·5 to 1·55.

Carborundum has a true specific gravity of 3·17–3·21. The true specific gravity of other forms of carbides and carboxides are as follows :—

Silundum	3·0
Siloxicon	2·52
Fibrox	1·8–2·2

Fibrox has a remarkably low apparent density, as about 99 per cent. of its volume is air.

Chromite has a specific gravity of about 4·5 ; bricks made from it have an apparent density of 3·0 to 3·2.

The Determination of Specific Gravity, Apparent Specific Gravity, Apparent Density, and Volume-Weight

Various methods are available for determining the true and apparent specific gravity and the volume-weights of ceramic materials. It is necessary to select the one which is the most convenient for the particular material to be examined, and for this reason the various methods are divided into groups according to the information desired and the state of the material.

The **volume-weight** of any powdered material or fluid is determined by measuring a convenient quantity of the material and then weighing it. If a sufficiently large volume can be treated in this manner the results are fairly accurate, but for small quantities special precautions must be taken to ensure the volume being measured accurately. For instance, if the volume-weight is to be expressed in " lbs. per cubic foot," and a box or other vessel of exactly one cubic foot capacity is available, it is merely necessary to weigh this vessel when empty and then when filled with the material. The difference in weight at once gives the desired volume-weight. If only a smaller vessel is available it should be weighed first empty (E), then filled with the material (=S). The vessel should then be emptied, filled with water, and again weighed (=W). Then

$$\text{The volume-weight (in lbs. per cub. foot)} = \frac{S-E}{W-E} \times 62{\cdot}3.$$

If the volume-weight is desired in grammes per litre, a litre flask [1] should be weighed empty and again when filled to the mark on the neck with the material to be examined. The difference between the two weights will give the volume-weight in the desired terms. In all determinations of the volume-weight of powders the looseness of the packing affects the result, and all " ramming " or tamping should be avoided.

If the volume-weight of a single solid mass is required some means must be found for measuring its total volume, including pores. If the mass is sufficiently large and symmetrical in shape its volume may be calculated from its length, breadth, and height, or in accordance with other appropriate mensurational method, but if it is very irregular in shape, some kind of volumeter (p. 84) must be used. In measuring the volume of a solid substance by means of such a device it is often convenient to weigh the water instead of measuring it and to calculate the volume of the water from the fact that each 1 oz. of water weighs one-thousandth of a cubic foot, or, which is slightly more accurate, that 1 cubic foot of water weighs 997 oz.

Instead of measuring the volume of a solid directly, an indirect method may be used when the substance is quite free from pores. In that case, the piece of material is suspended from one arm of a suitable balance by means of a thin thread and is weighed. It is then immersed in water, and whilst so immersed and still suspended by the thread it is again weighed, then

$$\text{Volume-weight} = \frac{\text{Weight in air}}{\text{Loss of weight in water}}.$$

If the volume-weight is required in lbs. per cub. foot, the above result must be multiplied by 62·3, or by 1000 if it is required in grammes per litre.

This method is inapplicable to porous materials, because the water would enter the pores and so give an erroneous result.

When the volume-weight of a liquid is required in terms of " ounces per pint," it is usually best to counterpoise on a balance an empty pint vessel, the accuracy of which has previously been certified by an inspector of weights and measures. The

[1] Determinations made on very small quantities are unreliable.

vessel is then filled with the liquid and weighed, the weight in ounces giving at once the desired information.

The errors in all the foregoing methods depend chiefly on the accuracy with which the weighings and measurings can be made. It should not be difficult to weigh even a comparatively large mass to within $\frac{1}{1000}$ of its true weight, and with smaller quantities a much greater relative accuracy can be obtained by the use of a suitable balance. A greater error is usually made in the measurement, especially if the vessel has a wide mouth. For this reason, flasks with narrow necks are preferable, as the risk of serious error is much less. Such flasks often introduce another error when used for powders, as it is almost impossible to fill them completely without so much shaking or tilting of the flask as will have an undue consolidating effect on the powder.

In determining the "weight per pint" of glaze slips, etc., an error of $\frac{1}{4}$ oz. is generally disregarded by the workmen concerned. A much more accurate result can be obtained by the use of a flask with a narrow neck.

The **apparent density** is conveniently determined in a suitable quantity of material in the following manner :—

(*a*) In the case of a non-porous substance, by weighing it first in air and then in water, as described on p. 222. Then :

$$\text{Apparent density} = \frac{\text{Weight in air}}{\text{Loss of weight in water}}.$$

(*b*) By weighing the material, placing it in water or other suitable liquid until it is saturated, and afterwards transferring the saturated material to a volumeter in which its volume can be measured.

This instrument has various forms : one of the most convenient being described on p. 84. The apparent density is then found from the formula :

$$\text{Apparent density} = \frac{\text{Weight in grams}}{\text{Volume in cubic centimetres}}.$$

A volumeter can sometimes be improvised by using a tall glass jar containing a suitable quantity of water which reaches to a mark on the glass. The vessel and water are weighed, the saturated sample is carefully placed in the jar and the height to which the water rises is carefully marked on the glass. The jar is then emptied, filled again with water to the upper mark and again weighed, the increase being the weight of a volume of water equal to that of the sample.

When saturating a porous body in order to fill its pores and so enable its total volume to be measured in a volumeter, it is often preferable, where possible, to use an oil, such as paraffin or turpentine, as these penetrate more rapidly than water into the pores of the articles and ensure them being filled more completely.

(*c*) The apparent density may be calculated by the following formula due to S. Wologdine and A. L. Queneau [1] :—

$$\text{Apparent density} = \frac{Ps}{Pm - Pe},$$

[1] *Electrochem. and Metall. Industry*, Oct. 1909.

where the weight of the dry sample=P*s*, the weight of the sample saturated with water=P*m*, and the weight of the sample immersed in water=P*e*.

(*d*) The apparent density of a symmetrical mass of simple form may also be determined with fair accuracy as described on p. 222, *i.e.* by weighing the mass, calculating its volume from the product of its length, breadth, and height, or by applying the appropriate mensurational method and then calculating the weight of an equal volume of water. The weight of the mass divided by the weight of an equal volume of water will be its apparent density.

The **apparent specific gravity** is determined by the following formula :—

$$\frac{\text{Weight in air}}{\text{Vol. of mass} - \text{Vols. of open pores}}.$$

The volume of the mass may be determined by any of the methods (*b*), (*c*), or (*d*), described in the section on " apparent density " (p. 223), whilst the volume of the open pores may be determined by the methods described in Chapter II under the heading *Porosity* (p. 81).

The **true specific gravity** may be determined by several methods, according as the material under examination is a solid mass, a powder, or a liquid.

The true specific gravity of a *non-porous* solid may be determined by—

(*a*) Weighing a piece of the solid and then suspending it in water and re-weighing it (see p. 222). The specific gravity is found by dividing the weight of the material by its loss of weight in water, *i.e.* specific gravity=P*s*÷P*s*−P*e*, where the weight of the dry sample=P*s* and the weight of the sample immersed in water=P*e*.

(*b*) Weighing a piece of the material, measuring its volume in a volumeter (p. 84), and dividing the weight (in grammes) by the volume (in c.c.).

The true specific gravity of a *porous* solid may be determined by—

(i) By method (*a*) above.

(ii) By method (*b*) above, but using the volume of the sample, after deducting the volume of the pores which can be filled by saturating the sample with water.

Neither of these methods will be accurate if the material contains any sealed pores (p. 204). In fact, method (ii) is identical with that used for determining the apparent specific gravity of a material containing sealed pores. With such materials, method (iii) must be employed.

(iii) Grinding the material to a fine powder, the individual grains of which are too small to contain any pores and determining its specific gravity (see *below*).

Vitrified materials are anomalous, because they may appear to be non-porous and yet may contain many sealed pores. Hence, they should be ground to a very fine powder before their specific gravity is determined, as unless the sealed pores are broken low results will be obtained.

The true specific gravity of a powder may be determined by means of a specific-gravity bottle or pycnometer.

The bottle and stopper are cleaned, dried, and weighed (=P); a sufficient quantity of the dry powder to half fill the bottle is placed in it and the bottle is again weighed (=W); the increase in weight is the weight of solid material used

$(=W-P)$. The bottle is completely filled with water,[1] the stopper inserted, any surplus water is removed, and the bottle with its contents is weighed $(=W_2)$. The bottle is emptied, cleaned, refilled with water, and weighed $(=W_1)$. The specific gravity is then found by using the formula :

$$\text{True specific gravity} = \frac{W-P}{(W_1-P)-(W_2-W)}.$$

The results of duplicate determinations should agree within 0·005. Where the solid is affected by immersion in water some inert liquid must be employed, the formula then being :

$$\text{True specific gravity} = \frac{(W-P)S}{(W_1-P)-(W_2-W)},$$

where S is the specific gravity of that liquid.

Le Chatelier and B. Bogitch [2] recommend a rapid method for measuring the specific gravity of powders which consists in dropping 8 grams of the material into a tall graduated glass containing a liquid which easily wets the surface of the powder (*i.e.* carbon tetrachloride, benzene, or paraffin) and noting the change in volume, which is read accurately to $\frac{1}{100}$ c.c. by means of a magnifying glass, and is the volume of the material.

A similar method, devised by Stanger and Blount, consists in using a graduated pycnometer (fig. 15) into which 50 c.c. of an inert liquid (water is generally satisfactory) are placed by means of a pipette, and also exactly 50 grams of the solid material. After shaking gently to remove any air bubbles, the volume is read off on the neck of the bottle and the specific gravity is calculated from the formula :

$$\text{Specific gravity} = \frac{50}{(\text{pycnometer reading}-50)}.$$

Fig. 15.
Specific Gravity Bottle.

The true specific gravity of a *paste* or highly-plastic clay is very difficult to determine. Method (*b*) on p. 224 may be used, though it is often difficult to transfer the whole of the clay to the volumeter. This difficulty may be avoided by weighing more clay than is required, transferring a portion of it to the volumeter and re-weighing the residue ; the difference in weight is that of the paste used in the volumeter. Many pastes retain air very tenaciously and only part with it when mixed with a very large volume of water. Hence, for very accurate work, it is necessary to determine the volume of the paste (including air) as just described and then, by mixing it with water, to liberate, collect, and measure the air contained in the sample and to deduct the volume of the air from that of the paste. The true specific gravity of the paste is then found by dividing its weight by the corrected volume.

[1] If necessary, the bottle and its contents may be boiled and subjected to vacuum in order to expel all air from the powder.

[1] *Rev. de Métal.*, **15**, 511 (1918).

The true specific gravity of a *liquid* may be determined—

(*a*) By immersing a suitable hydrometer in the liquid and noting the figure on the hydrometer which coincides with the surface of the liquid. In thick, viscous liquids—such as slips—hydrometers are not very accurate. Where they are used, care must be taken that the hydrometer does not touch the bottom of the container and the eye of the observer in reading the hydrometer should be as nearly as possible on a level with the surface of the liquid.

(*b*) By means of a Westphal balance, in which a glass plummet is immersed in the liquid and " weighed " in that position. Special weights are used which enable the specific gravity to be read off directly and without calculation.

(*c*) By means of a specific gravity bottle or pycnometer. The dry empty bottle and stopper are weighed (=B); the bottle is filled with the liquid, the stopper inserted, any surplus liquid being removed, and the bottle with its contents is again weighed (=L). The bottle is then emptied, cleaned, dried, filled with water, and again weighed (=W). Then

$$\text{True specific gravity} = \frac{L-B}{W-B}.$$

The last-mentioned method may be modified by using any convenient vessel, but for really accurate results it should have a neck. For many purposes, a pint measure may be used; it is weighed empty, then when filled with water and again when filled with the liquid. The specific gravity of the liquid is found by dividing the weight of 1 pint of it by the weight of 1 pint of water.

The weight of solid matter in a pint of slip is equal to $(P-20)\frac{G}{G-1}$, where P is the weight of the slip in oz. per pint and G is the specific gravity of the dry substance. If G is 2·6, as is the case with many ceramic materials, the weight of solid matter in a slip is $(P-20)\times 1{\cdot}625$. Conversely, the weight (in oz.) of a pint of slip is $20+\frac{W(G-1)}{G}$, where W is the weight of dry material per pint and G is the specific gravity of the dry substance.

Many glazers do not determine the specific gravity or volume-weight of the slips they use, but judge their consistency by merely placing their hand and arm in it or by dipping a piece of burned clay into the slip and then scratching the coated surface with the finger nail, the nature of the scratch indicating the satisfactoriness or otherwise of the slip. Such methods are obviously too crude to be really satisfactory, yet they are extensively used.

It should be noted that the true specific gravity and the apparent density are identical when the substance under examination is a powder, a non-porous solid, or a liquid. They only differ in the case of porous solids.

CHAPTER VI

CHANGES IN THE PHYSICAL STATE EFFECTED BY WATER

Ceramic materials are found in several different physical states, namely :—

(*a*) A solid mass of varying hardness and comparatively rigid.

(*b*) A plastic or " malleable " paste which is capable of being moulded to any desired shape.

(*c*) A fluid slip which can be poured from one vessel into another.

In making any ceramic articles there are five stages through which the raw material must pass :—

(*a*) The preliminary treatment of the raw materials, so that they are in a suitable physical condition to facilitate the next stage of preparation. This is chiefly effected by the process of *weathering*.

(*b*) The preparation of a paste, powder, or slip of the required consistency.

(*c*) The shaping of the articles.

(*d*) The drying of the articles.

(*e*) The burning or firing of the articles, which is described in Chapter XIII.

In order that a ceramic material may be used it must, therefore, be treated with water in order to provide a suitable product ; the latter must be given the desired shape and any surplus water present must be removed by drying, preferably before the articles are sent to the kiln.

Water is the principal agency which is used to convert unfired ceramic materials from a rigid solid to a plastic paste or to a fluid slip, whilst heat and air are the principal agencies employed for converting a slip into a plastic paste or a paste into a rigid solid. The present chapter deals with the physical changes which result from the action of water on clays and other ceramic materials, such water being present naturally in the raw materials or purposely added to them in order to give them a desired consistency or other properties.

As the ceramic material which is most susceptible to the action of water is clay, this chapter deals principally with the properties of clay. Most of the other ceramic materials are almost inert to the action of water and cannot, by the mere addition of it, be converted from a rigid solid mass into a paste suitable for the manufacture of different kinds of articles. They must usually be mixed with some other material before they can produce a suitable paste.

If a piece of clay is placed in a large volume of water, the latter will gradually permeate the former, loosening and separating the particles, until the mass " slakes,"

or falls to pieces. The disintegration may be hastened by grinding or stirring the clay and water and, if they are sufficiently well mixed together, a " slip " or " slurry " is obtained. If the amount of water used is only about one-fifth of the weight of the clay and the mixing is sufficiently thorough, a plastic paste is produced. This paste can be hardened by drying it, or it can be converted into a slip by mixing it with an equal weight of water.

At first sight the action of water on clay appears to be simple ; if only a little water is present, the particles of clay adhere well together and the solid mass increases in softness roughly in proportion to the water present. If a large excess of water is added, the particles of clay are separated from each other and again their behaviour appears to be easily understood. On investigating the matter still further, however, it is found that clay is the only natural mineral which possesses in so high a degree the property of plasticity, and a still further investigation will show that clays possess many other unusual physical properties ; some of these properties are possessed by complex organic substances such as gums, resins, glue, etc., but clays differ from the latter in not being completely consumed when heated in a current of air. Plastic materials of an organic nature are wholly destroyed by heat, but clays are converted thereby into hard, stone-like bodies. These special properties of clays bear so close a resemblance to those of a larger class of substances known as colloids (p. 10), that it is commonly understood that plastic clays contain a considerable amount of colloidal matter. Whether this is so or not has yet to be proved, for only insignificant quantities of colloidal matter have been definitely separated from the purer clays. The similarities between plastic clays and colloidal substances are so numerous, however, and so many of the properties of such clays can be explained so much more satisfactorily by assuming these clays to be colloids that, without some knowledge of colloidal phenomena, it seems almost impossible to fully understand many of the properties of clays and phenomena exhibited by the interaction of clay and water.

Colloidal Phenomena

The nature of materials in the colloidal state has been briefly outlined on p. 10. In the following pages the properties of colloidal sols and gels are dealt with more fully in order that their application to ceramic materials may be properly understood.

Properties of Colloidal Sols.—The principal properties possessed by colloidal sols are as follows :—

Electric Charge.—All colloidal particles bear a charge of electricity which may be either positive or negative according to the nature of the colloid. The stability of the sol is largely dependent on the electrical charges of the particles. So long as all electrolytes and sols in a given sol have like electric signs, the sol is stable, but if any particles having a charge of opposite sign are introduced, coagulation occurs. The charge appears to depend largely on the environment of the suspended particles, though oxides, hydroxides, and sols of readily-oxidised materials usually bear a positive charge, whilst materials which are not readily oxidised usually bear negative charges. This " rule " is by no means exact, as silica, clay, and humus bear negative

charges, whilst alumina, ferric oxide and hydroxide, lime, magnesia and the hydroxides of chromium, copper, aluminium, zirconium, titanium, etc., are positively charged. The electric charges possessed by colloidal particles give rise to a phenomenon termed *kataphoresis*, namely, that in an electric field the colloidal particles move in a direction which is determined by their respective charges, negatively charged particles travelling towards the anode and positively charged particles passing to the cathode.

Helmholtz suggested that, when a particle suspended in a liquid becomes charged electrically, there exists about it a double layer. When the particle is negatively charged there is a layer of negative electricity on the surface of the particle and a corresponding layer of electricity in the liquid immediately surrounding the particle. Hence, the centre of gravity of the complete system of solid particles surrounded by the charged layer of fluid cannot be moved by the electric force in the fluid, except so far as the latter tend to bring about a displacement of the two oppositely charged layers. This could not occur if the liquid were a perfect insulator, but as it is not so, the particles are transported to the corresponding electrodes. The rate at which the particles travel is similar to that of the ions in a true solution. It has been calculated by Lamb as—

$$v = \frac{\mathrm{X}el}{4\pi a^2 n}.$$

X = gradient of electrical potential in the liquid.
e = charge on the particle.
a = radius of particle.
n = coefficient of viscosity.
$l = \frac{n}{\mathrm{B}}$ where B = coefficient of sliding friction of the fluid in contact with wall of the cell; l usually $= 10^{-8}$ cm.

It can be shown that the mobility of a particle is independent of its radius and that nv is constant for a given solution. When a charged particle reaches an electrode of opposite sign it usually gives up its charge and is deposited, but it may take up the charge of this electrode and travel towards the other electrode. Small changes in the concentration of H° or OH' in the electrolyte produce large changes in the solid and may effect reversal of migration.

On prolonged kataphoresis, traces of electrolyte accumulate at the electrodes and decrease the H° at the cathode and increase it at the anode, causing the cathode liquid to be alkaline and the anode liquid to be acid, with corresponding changes in the charges on the particles. Sometimes the particles with a reversed charge touch some original particles, both losing their charges and being precipitated.

With a heavy current, a charged particle may be attracted to an electrode of the same sign. The assumption that, in an electric field, the colloid particle assumes a charge of one sign and the surrounding liquid a charge of the opposite sign correlates the phenomena of kataphoresis with those of electro-osmosis, but does not explain the fact that basic colloidal particles become positively charged, but acid and neutral particles negatively charged. These facts are accounted for, according to Noyes, by

assuming the phenomenon to be one of ionisation. Thus, each aggregate of ferric hydroxide may dissociate into one or more hydroxyl ions and a residual, positively charged colloidal particle and each aggregate of silicic acid into one or more hydrogen ions and a negatively charged colloidal particle. In the case of quartz and other neutral substances, it must be assumed that the water or other electrolyte is ionised.

The exact value of the charge in a colloidal particle has not been accurately ascertained.

The phenomena of kataphoresis is also shown by certain soluble substances termed electrolytes, but never by inactive suspensions of solid matter in a liquid.

Electro-osmosis is another electrical phenomena exhibited by colloids. If a negatively charged sol is contained in a vessel in which a porous pot or diaphragm is partly immersed and an electric current is passed in such a manner as to transport the negative particles towards the anode on the interior of the vessel or on the farther side of the diaphragm, or if the diaphragm itself forms one electrode, the negatively charged particles will be deposited on the anode, but the water which is intimately associated with the suspension will pass to the cathode so that the suspended matter and the water will be separated from one another. The rate at which the separation takes place is proportional to the current used.

Electrical endosmose, according to T. R. Briggs, is dependent on the preferential or selective adsorption of ions and is influenced only by those ions which are adsorbed by the diaphragm. The electrical endosmose depends on the condition of the surface of solids and on the ion-concentration. The direction of endosmose indicates the sign of the diaphragm and the rate of flow will be proportional to the intensity of the charge on the diaphragm. The adsorption of cations tends to produce positive diaphragms, whilst anions tend to produce negatively charged diaphragms. When both occur, their charges are neutralised.

I. M. Kolthoff[1] considers electro-adsorption to be purely a chemical phenomenon, in which one ion of a very slightly soluble salt is replaced by another ion to form a second difficultly soluble salt similar to the base exchanges in permutite.

Perrin has found that electro-osmosis only occurs with ionising liquids (*i.e.* those with a high dielectric constant) and that of these, feebly acid liquids gave a positive charge to the walls of the diaphragm (*i.e.* the liquid moved toward the positive electrode), whilst in a feebly alkaline medium the walls became negatively, and the liquid positively, charged. Particularly strong effects were shown by the strong acids and bases and by solutions of salts with polyvalent ions.

The **electrical conductivity** of colloidal sols is greater than that of water, but less than that of a similar quantity of material in a truly dissolved state.

Electrical Precipitation.—When two colloidal sols of opposite electric charge are mixed, they mutually precipitate each other, the particles being attracted to one another and, in coalescing, form larger masses which settle rapidly. The effect depends greatly on the manner and rate at which the second colloid is added, but if the mixing is effected rapidly Bilz found :—

(i) A small proportion of added colloid produces no precipitation.

[1] *Koll. Zeit.*, **30**, 35–44 (1922).

(ii) As the proportion of added colloid is increased, the coagulative action is increasingly noticeable until a proportion is reached which causes immediate precipitation.

(iii) A great excess of the added colloid may prevent precipitation.

(iv) Mixing two colloids of the same sign does not cause coagulation.

It is, therefore, clear that the coagulation is due almost wholly to electric action.

The proportion of each colloid in the precipitate is constant and many reactions formerly thought to be chemical are probably electrical precipitates.

Precipitation by Electrolytes.—Colloidal sols are also precipitated by solutions of electrolytes carrying opposite electric charges to those of the colloidal particles. For this reason, unless special precautions are taken, colloidal sols are seldom very stable, very small amounts of impurity serving to precipitate them and destroy their value. This phenomenon does not depend on the chemical properties of the electrolyte, but on their introducing an electric charge of opposite sign to the colloid. The activity of electrolytes is in proportion to the valency of the liberated ions, solutions of salts of trivalent ions having a much greater effect than those of mono- or divalent ions. Freundlich concludes that the coagulative power of a salt depends on its valency and its adsorption coefficient, because with different ionic values of either valency or absorption very different concentrations are necessary in order that the equivalent quantity of the active ion shall be absorbed. Wo. Ostwald, on the contrary, denies the influence of valency.

Burton has pointed out that the effect of the ions having the same charge as the colloid must not be overlooked, especially as when a univalent ion is used for coagulation, another ion of equal or greater valency is present, whereas when a trivalent ion is used, the other ion is usually of less valency and may have a peptising effect which upsets all theories based on experiments where its action has been disregarded.

If an electrolyte is added systematically, an *iso-electric point* will be found, after which the addition of more electrolyte will have the opposite effect and will increase the stability of the sol. The most rapid coagulation occurs when the amount of electrolyte added is just enough to ensure complete coagulation, *i.e.* at the iso-electric point. If an excess is added, the particles adsorb the ions and the charge on the particle is reversed.

According to H. D. Murray,[1] the precipitation of colloids by electrolytes is dependent upon (*a*) the specific action of ions of opposite electric charge, (*b*) the greater effect of higher valency; (*c*) the modifying action of ions of the same sign as the colloid; (*d*) the possible adsorption of equivalent quantities of ions; (*e*) the minimum necessary concentration of the electrolyte; and (*f*) the possible effect of an ion originally present.

According to O. Ruff,[2] coagulation is caused by the replacement of the dispersion medium by molecules of the coagulant or by the stronger attraction of the coagulant for the dispersion medium, or it may be due to the adsorption of ionised particles of opposite sign causing loss of electric charge and thus the shell of the dispersing medium.

Recent work by Mayer, Schaeffer, and Terrome has shown that the addition of

[1] *Chem. News*, **123**, 277–9 (1921). [2] *Koll. Zeit.*, **30**, 356–364 (1922).

traces of alkali increases the size of positively charged colloidal particles and of reducing the size of those negatively charged. The addition of traces of acids has the opposite effect.

The results of recent work on coagulation may be summarised as follows :—

(*a*) The presence of a very minute quantity of electrolyte does not lessen the number of particles of colloid in suspension.

(*b*) The addition of a small quantity of electrolyte may increase the number of submicrons of colloid at the expense of its amicrons.

(*c*) The electrolytic coagulation of a colloid composed of particles of various sizes occurs first by the aggregation of small particles with larger ones and not by the aggregation of particles of equal sizes, *i.e.* the larger particles act as condensation nuclei of the smaller ones.

Many—but not all—coagulated colloids can be again dispersed by the reverse action to that which causes their coagulation, *i.e.* if precipitation is caused by the addition of positive ions, deflocculation will occur when negative ions are added in excess of the positive ions.

The precipitates obtained from colloidal sols may be :—

(i) *Crystalline*, without any colloidal characteristics ;

(ii) *Sandy* or dense (as opposed to a flocculent or spongy precipitates) and usually formed by agglomeration of a flocculent precipitate ;

(iii) *Flocculent*, light or spongy precipitates which do not settle readily and usually include a large proportion of water. Many gels are of this type ;

(iv) *Gelatinous*, *jelly-like*, or viscous, as aluminium hydroxide and differing from a true jelly in showing a distinct liquid phase ;

(v) *Curdy*, or resembling the curds produced by adding an acid to milk ;
and

(vi) *Liquid*.

The size of the precipitated particles depends on the conditions under which they are formed. If produced from highly-concentrated solutions, the precipitates are usually flocculent or crystalline. If gelatin or some other substance which is strongly adsorbed by the precipitate is present before and during precipitation the precipitate will be in a finely-divided state. Slow precipitation, especially under favourable conditions of temperature, usually favours the formation of a coarsely crystalline precipitate. The presence of ions of a particular type may also affect the nature of the precipitate.

Protection.—When a stable colloid, such as gelatin, and a less stable colloid of the same electric sign are acted upon by an electrolyte of opposite sign which is sufficiently concentrated to coagulate the less stable colloid, but not the more stable one, the latter may act as a protective agent and prevent the coagulation and precipitation of the less stable colloid. In this way, an unstable colloidal sol may be protected by the addition to it of a more stable colloid, the mixture being less liable to coagulation than the original colloid. The black colloidal matter found in soils (*humus*), gelatin, peptone, and many organic colloids, are very effective protective agents and prevent precipitation or flocculation.

Protective colloids play an important part in many colloidal reactions. The exact mode of action of protective colloids is not well understood ; it offers some of the most perplexing problems in chemistry.

Many colloidal sols are made stable by absorbing a minute quantity of salts or acids. Thus, stable silicic acid sol always contains traces of potassium, sodium, and chlorine, whilst stable ferric hydroxide sol contains a trace of ferric chloride. If these traces are removed by dialysis the sol is rendered unstable.

Moore and others hold that when the electrolytes are removed from colloids, the latter are denatured or polymerised, with resultant coagulation, and they maintain that such electrolytes are essential to the stability of the colloidal sol state.

Brownian Movement.—When active colloidal sols are examined by means of an ultramicroscope, the particles are seen to be in a state of violent irregular motion, both the speed and direction of motion of the particles being very irregular ; it has been shown by Gouy, Perrin, and others to be due to the bombardment of the particles by the " molecules " of the liquid, but as the latter are far too small to be seen, even with an ultramicroscope, only the colloidal particles appear to be in motion. According to Zsigmondy [1] particles larger than 0·00015 inch show no perceptible Brownian movement and active movement is confined to particles less than 0·000004 inch diameter.

The distribution of particles showing the Brownian movement, their velocities and the frequency of their collision, is the same as the kinetic theory assumes to be the case with particles of a gas.

According to Sven Oden, the stability of a suspension is not dependent upon the Brownian movement and this movement may even facilitate deposition by bringing the particles within each other's range of molecular attraction. When an acid is added to a clay suspension, the Brownian movement still continues until the particles are coagulated.

The **osmotic pressure** (or force exercised on a diaphragm which forms part of a vessel immersed in the sol) of colloids is very small and is not, as in true solutions, proportional to the molecular weight of the dissolved substance. Failure to recognise this difference has led to foolish statements respecting the " enormous molecular weights " of some colloids.

Some colloids when in a state of high dispersion possess a recognisable osmotic pressure, but this is unusual, though it follows as a consequence of the existence in them of the Brownian movement and of their diffusibility.

The osmotic pressure of colloids is very inconsistent. Different preparations of the same colloid give different results, and shaking, stirring, standing, etc., all affect the osmotic pressure.

Acids and alkalies may either increase or decrease the osmotic pressure of colloids. Sometimes one colloid will show both types of behaviour. The addition of alkali usually increases the osmotic pressure to a maximum, after which it falls again.

[1] *Kolloidchemie*, 1912, p. 18.

Low concentrations $\left(\text{under } \frac{N}{2500}\right)$ of acid produce only a slight osmotic pressure, but higher concentrations $\left(\text{under } \frac{N}{400}\right)$ cause an increase which rises steadily.

The addition of *salts* decreases the osmotic pressure, the neutral salts of the alkali metals causing the smallest decrease. The salts of the alkaline earths and those of the heavy metals are most effective.

In solutions, the osmotic pressure is directly proportional to the absolute temperature and to the number of molecules in unit volume of the solutions at constant temperature (J. H. van't Hoff's law). Sv. Arrhenius assumed dissociation into ions when a gram-mol in unit volume shows an osmotic pressure above that calculated.

In colloids, the degree of dispersion, the type of dispersed phase, the degree of hydration, etc., all affect the osmotic pressure.

With any given substance in a given dispersion medium, each particle behaves as a molecule, and if N particles (Avogadro's number) are present in unit volume, the system will exert unit osmotic pressure.

The variations in osmotic pressure of a colloid under different conditions are due to " changes of state "—especially in its degree of dispersion and its type. The osmotic pressure of colloids is thus not merely a function of the number of particles in unit volume, but varies with the changes in the state of these systems, especially with the changes in the degree of dispersion and the type of the dispersed phase. Hence, it is impossible to assign absolute values to the osmotic pressure of colloidally dispersed systems.

Diffusivity.—Colloidal sols diffuse through membranes much more slowly than true solutions, their diffusivity being almost zero. This property is used in the process of dialysis to separate dissolved salts from colloidal sols.

The **specific gravity** of colloidal sols is directly proportional to the amount of colloidal matter in suspension, but does not follow the ordinary laws of suspensions.

The **viscosity** of colloidal sols is that property which prevents them flowing as freely as water through a small orifice. Ostwald [1] states that the viscosity of a colloidal substance depends upon its (*a*) concentration ; (*b*) temperature ; (*c*) degree of dispersion ; (*d*) solvate formation ; (*e*) electric charge or ionisation ; (*f*) previous thermal treatment ; (*g*) previous mechanical treatment ; (*h*) presence of small quantities of other more viscous colloids ; (*i*) age ; and (*j*) presence of electrolytes or non-electrolytes.

The viscosity of sols is usually negligibly greater than that of the dispersing medium (" solvent ") unless the concentration is so great that the mass of disperse solid phase predominates over the dispersing medium. Hence, the viscosity rises very slowly at first, but very suddenly and greatly with high concentrations. The viscosity of sols of alumina, silica, and some silicates is much greater than that of the corresponding solutions.

The addition of a suitable electrolyte reduces the viscosity of a colloid sol, but

[1] *Trans. Faraday Soc.*, **9**, (1913).

increases the viscosity of a true solution. The reduction sometimes requires several days and is accompanied by coagulation. The viscosity of emulsoids usually increases with small doses and decreases with larger ones. The viscosity of emulsoids is reduced by mechanical stirring.

Reversibility.—When sufficient care is taken, colloidal sols may be dehydrated so as to form a dry gel and then rehydrated so as to pass again into the sol state, no change apart from the loss of water taking place. If the temperature is raised too much, however, chemical changes may occur and the gel may become set. If the degree of dispersion can be increased, or decreased, by reversing the conditions which brought about the change, the dispersoid is said to be a *reversible* colloid; otherwise it is termed *irreversible.*

Properties of Colloidal Gels.—Many of the properties of colloidal sols apply equally well to colloidal gels, as a gel is merely a coagulated sol. Colloidal gels are always very viscous and it is generally agreed that they have a honeycomb structure similar to a sponge, but Zsigmondy has shown, and his work is supported by Barratt, that some gels consist of a mass of intersecting fibrils united at the points of intersection, and it has been suggested that in some cases these fibrils may be crystalline. The amount of water they contain determines their nature; thus, silica gel may contain up to 300 molecules of water to each one of silica. Such a gel, if broken, will unite again; a gel with 30 to 40 molecules of water to one of silica will stand alone; one with 20 molecules is stiff; with 10 molecules it is brittle and with only 6 molecules it can be ground to powder.

Absorption.—Colloidal gels are capable, on account of their spongy structure, of absorbing very large quantities of water with a slight evolution of heat. Many of the phenomena described under "adsorption" (*below*) are related to the apparently gel-like structure of clays.

Contraction.—On account of the large amount of water they contain, gels, on drying, contract very greatly and often crack badly. The drying commences at the surface and proceeds at a rate depending partly on the nature of the atmosphere and partly on the capillary structure of the mass of the gel, the liquid being drawn through the capillary tubes to the surface of the gel where it is evaporated and removed.

If the dry mass is again exposed to the action of water, it can be largely, yet seldom completely rehydrated according to the nature of the gel.

Action of Heat.—When gels are heated to a temperature above 100° C. they crack badly, their water is wholly removed and they lose most of their colloidal properties and are largely converted into irreversible gels.

Adsorption.—Colloidal gels are capable of adsorbing various substances, these being so strongly held that they cannot be removed entirely by the ordinary washing process without converting the gel into the sol state, and even then it is sometimes impossible. Van Bemmelen describes adsorption as a phenomenon by which particles are retained by the surface of a material in contradistinction to absorption in which particles are distributed uniformly through the volume of the material.

Whitney and Ober have found that ions of electrolytic solutions are adsorbed by colloids in amounts exactly proportional to the electro-chemical equivalent weights

of these ions, and Freundlich has further found that, for a given colloid, ions of differing valency are absorbed equally strongly in equimolecular concentrations of the ions in solution. The characteristic equation for adsorption [1] is

$$\frac{x}{a} = KC^m,$$

where x=amount of dissolved substance adsorbed ;
a=amount of adsorbing substance ;
C=concentration of solution ;
K and m are constants.

The enormous power of adsorption possessed by colloids is due to their peculiar structure, which gives them a very great surface area and, consequently, they exhibit to a very marked degree various surface phenomena of which adsorption is one.

Certain solid substances which appear to possess some colloidal properties have the power to absorb gases or vapours. This absorption is limited to the surface of such materials, but as they are all porous their total surface is extremely large as compared with their external dimensions. Thus, some forms of charcoal will adsorb or condense in their pores (*i.e.* on their internal and external surfaces) more than one hundred times their volume of gases. The adsorption is sometimes extremely rapid and complete, *e.g.* a good gas mask will reduce 1000 parts of toxic gas per million parts of air to less than 1 part per million in the tenth of a second in which the air is inhaled through the mass. Clay also exhibits this adsorption phenomena to a less extent.

It is important to remember that all colloidal reactions have both a physical and a chemical aspect. Certain colloids have a special affinity for each other which is not purely chemical, but follows the (physical) laws of adsorption. The precipitation of a colloid may be regarded as an ordinary chemical precipitation or as taking place in two physical stages : (i) the reversal of sign by the addition of an acid, and (ii) flocculation by a colloid of opposite sign.

The whole problem of colloidal phenomena is a complex of physical and chemical actions, though in ceramic materials they influence the physical properties to a greater extent than the chemical ones.

Colloidal Properties of Clays

Many of the properties mentioned on pp. 228–236 as characteristic of colloidal substances are equally characteristic of clays. Hence, the more important properties of a colloidal nature possessed by clays are described on the following pages.

Hydrolysis.—Water has a hydrolising action upon clay particles and may produce active colloidal particles, the material approaching nearer and nearer to a colloidal sol as the percentage of hydroxyl ions increases, until a suspension is finally produced. This action occurs very slowly and, consequently, slightly plastic clays cannot be greatly increased in plasticity by artificial hydrolysis, although a noticeable change may be observed when a clay-slip or sol is boiled under a reflux condenser for

[1] Freundlich and Losev, *Z. f. physik. Chem.*, **59**, 284 (1907).

many hours, the clay gradually becoming more plastic as a result of its hydrolysis by the water. A high temperature is not needed if sufficient time is available; thus, china clay which is treated in settling pits is more plastic than when artificially de-watered by other means.

As would be expected, the hydrolysis of clays is more apparent in the case of fine grains than with coarser ones on account of their greater surface area. Thus, finely divided silica can be rendered colloidal by prolonged boiling with water, whilst coarser grains are not appreciably affected.

W. and D. Asch [1] consider that hydrolysis consists in the formation of larger molecules by the addition of the elements of water to the clay molecules. This view is also held by W. H. Lewis,[2] but Purdy denies that any hydrolysis occurs as the result of the action of water on clays.

Hygroscopicity.—As mentioned on p. 227, clays are capable of absorbing a large quantity of water; this is a phenomenon and is equivalent to the swelling of colloidal gels (p. 235), and J. Splichal [3] has suggested that the amount of colloidal matter in a clay may be estimated from its hygroscopicity.

The swelling of clay in water is best understood as a change whereby the clay enters into physico-chemical combination with the water, but is distinct from "solution"; the latter is preferably regarded as an increase of the degree of dispersion of the particles of the "soluble matter" in the liquid.

Dehydration.—One of the chief arguments in favour of the view that clays are largely colloidal in character is the manner in which they lose water on drying in a desiccator. This subject has been carefully investigated by Van Bemmelen, who found that definite recognisable hydrates have a vapour tension which remains constant so long as the hydrate is present, but that aluminium hydroxide, iron hydroxide, silicic acid and clays do not possess this property, but lose water steadily and can take it up again in the same manner.

In silicic acid and some clays, the loss of water is continuous except at some points in which there is loss of water without much change in the vapour-pressure, and suggests the possible formation of definite, but very unstable, compounds with water. The rate at which water is absorbed by clays and by silicic acid is very different from that at which water is lost, and this again suggests the possible existence of definite compounds. On the whole, however, the indications are that clays and some of the impurities associated with them are largely colloidal in character.

Indurated clays and shales are produced by the dehydration of the colloidal matter in clays. When these are subjected to the action of water they become rehydrated and their colloidal properties are again developed.

In this property of hydration and dehydration, clays resemble emulsoids rather than suspensoids, as the latter are not usually very readily reversible. Rehydration is only possible, however, if the molecules of clay have not been destroyed by the removal of any water, except that of formation and the hygroscopic water. If any

[1] *Silicates in Chemistry and Commerce*, Constable & Co., Ltd., London.
[2] *J. Soc. Chem. Ind.*, 1916, p. 12.
[3] *Zemedelsky Archiv, Prague*, 10, 413–31 (1919).

other change, such as a partial decomposition of the clay, has occurred, it becomes correspondingly more difficult to restore the plasticity of the clay, and if the clay has been heated to a temperature of more than 600° C., no method at present known is able to restore the lost quality. Purdy considers that dehydrated clay is not analogous to a set or dried gel as is sometimes supposed, but claims that the dehydration involves a change in chemical constitution and not merely of physical state.

Adsorption is a property possessed by plastic clays which is peculiarly characteristic of some colloidal materials (see p. 235). Particles of plastic clay are capable of adsorbing gases or vapours, liquids, and solids.

Adsorption of Gases and Vapours—Clay, precipitated silica, and alumina all adsorb gases and vapours to a small extent, the amount of adsorption varying with the gases or vapours, as well as with the adsorbent; thus, clay and dry precipitated alumina both strongly adsorb carbon dioxide and water vapour and, in 1909, Rohland reported that unsaturated hydrocarbon vapours are strongly adsorbed by clay. If a sample of clay is sufficiently dry and sufficiently fine, it will surge like a liquid, because the film of air around each particle acts as a cushion and enables the particles to move over each other as though they were suspended in a liquid. If the powder is heated, its mobility is still further increased, though the adsorption increases with a fall in the temperature of the dispersion medium.

The increased concentration of the adsorbed gas or vapour at the surface of a solid ought, theoretically, to increase the rate at which it can react, either with the solid or with other gases which may be adsorbed simultaneously. In the case of dry clay—which has an ample surface—the catalytic effect is not marked when the clay is cold and no experiments appear to have been made with it at moderately low temperatures. The effect of red-hot clay in decomposing carbon monoxide with the liberation of free carbon is well known. The power of dry clay to decompose ethyl alcohol, ethylene, and water is known, but the manner in which the reaction is brought about still requires explanation. It appears to be due to the increased concentration of alcohol adsorbed by the clay. The remarkable catalytic action of red-hot clay in causing a mixture of hydrogen sulphide and oxygen passed through it to form sulphur and water is due to a similar cause. It is used in the Claus-Chance process for the recovery of sulphur from alkali waste. As the same reaction occurs at a lower temperature in the presence of iron oxide, both this substance and burned clay are commonly used.

A similar phenomenon occurs in what is known as *surface combustion*, in which a mixture of coal gas and air is passed through a diaphragm formed of a porous mass of clay, and burns on the farther side of the diaphragm and raises it to a very high temperature, at which it becomes incandescent and radiates heat very intensely, thus forming a highly efficient heating appliance. W. A. Bone, who first investigated this subject, used fireclay diaphragms. China clay diaphragms are superior whilst efficient, but choke more readily as the pores are much smaller. Bone has reached the conclusion that the calcined clay adsorbs or condenses on its surface and in its pores both oxygen and hydrogen.

In all these cases, the dry clay behaves as a typical colloid, showing in a marked

degree the phenomena of gaseous adsorption which is a prominent characteristic of what are commonly regarded as solid colloids, *i.e.* those with a highly-viscous dispersion medium and a gaseous dispersed phase.

Adsorption of Liquids by Clay.—Clay behaves like a colloid in its power of adsorbing various liquids. In the first place, it is wetted by water, alcohol, and various other fluids, and for such " wetting " to occur the clay must adsorb the liquid more strongly than the air which was previously in contact with its surface and filling its pores. A piece of calcined china clay soaked in paraffin or alcohol adsorbs so much of the liquid that if the latter is ignited it will burn for quite an appreciable time.

The film of water adsorbed around each particle of clay has been estimated at 0·0000002 inch, and that around particles of quartz at about half this thickness. As the total quantity of water adsorbed by a piece of dry clay is quite appreciable, the total surface of the clay must be very large.

Clay adsorbs different liquids to a different extent, *i.e.* its power of adsorption is selective and under suitable conditions one liquid will displace another in contact with the clay. For the same reason, a greasy dish is readily cleaned by rubbing it with wet clay, and grease may be removed from wool and cloth by rubbing it with china clay. This use of china clay is important industrially in fulling cloth. When pressing bricks, tiles, and other clay-ware, the press-box and plunger are oiled so as to produce a wetted surface of oil and clay, which adheres to the metal far less than a surface of clay and water. The oil is adsorbed by the wet clay as well as by much dryer clay dust and thus provides the desired surface.

The power of clay to adsorb water when the ware is dipped in glaze slip—a coating of glaze being left uniformly distributed over the surface of the ware—is another phenomenon showing the colloidal nature of this clay both in the raw and calcined or fired state. The manner in which a piece of fired clay will adhere to the tongue is well known. This is due to the water being adsorbed by the clay and the air previously contained in the pores being displaced. The pressure exerted by the water appears to be about 5 atmospheres.

As the adsorption of water by clay must produce an exothermic reaction, it ought to be possible to measure the heat liberated when clay is wetted. This does not appear to have been done, and, though the rise in the temperature of a mixture of clay and water in a pugmill is very noticeable, it is not solely due to this cause.

Adsorption of Solids by Clay.—The power which plastic clays possess of retaining their plasticity when mixed with sand or other non-plastic material is a characteristic of some colloidal gels ; it is a special case of the adsorption of one solid by another. The clay is not distributed uniformly through the pores or interstices of the coarser particles, but most of it forms a coating on the non-plastic material and many of the pores remain unoccupied even though there is more than sufficient clay to fill them. Coarser particles have a much smaller surface and, consequently, have far less power of adsorption. The cohesion of plastic clay to iron and its much smaller adhesion to wood and zinc are additional examples of adsorption. When a thin film of oil is interposed between the clay and the metal no adsorption can occur, and the clay does not adhere. The fact that two plastic clays will not mix thoroughly

has been shown by Rohland to be due to the colloidal nature of the clays. The rates at which china clay is wetted by water and other fluids is due to a difference in the power of the liquids to displace the film of air previously adsorbed by the clay and to the power of selective adsorption possessed by the clay. This selective adsorption was also shown by Reinders and others, who shook dry china clay with water, then with one of a series of immiscible organic liquids. The particles of clay must be very fine, as coarse ones are inert. When clay is shaken with water and either carbon tetrachloride, chloroform, butyl alcohol, amyl alcohol, or paraffin, much of the clay remains suspended in the water, but an appreciable proportion collects at the interface of the two liquids. If the clay is shaken with water and benzene or benzolene, the greater part of the clay collects at the interface of the two liquids.

Adsorption of Solids from Solution.—One of the striking colloidal properties of clay is its power of withdrawing soluble salts from their solutions ; this is a case of selective adsorption.

As early as 1874, Bottiger showed that when an alcoholic solution of an aniline dye is shaken up with dry china clay or with kieselguhr and then with water, the liquid which can be separated by filtration is perfectly colourless, all the dye having been retained by the clay or kieselguhr.

M. A. Rakusin [1] has found that ordinary clays, when either dried or after calcination will decolorise a coloured petroleum spirit and will remove indigo from its solution in aromatic hydrocarbons, petroleum spirit, kerosene, or vaseline oil. Ashley proposed to make use of this phenomenon to measure the relative proportion of colloidal matter in various clays. For this purpose, he shook a weighed quantity (20 grams) of each clay to be tested with 1 gram of malachite green dye and 400 c.c. of water for one hour. The liquid was then allowed to settle over night and the amount of dye unadsorbed was determined by comparison with standard solutions of dye. The amount of adsorption and, therefore, of colloidal matter in the clay, is estimated from the reduction in the concentration of the solution of the dye. This is only correct so long as no liquid is retained by the clay, so that the method probably gives low results.

Arrhenius [2] found that dyes are adsorbed by clay in proportion to their molecular weights, the materials having the highest atomic weights being adsorbed to the greatest extent. Thus, Rohland [3] found that 15 grams of clay were required to adsorb a certain amount of vesuvin having a molecular weight of 227, whilst only one-third of this amount was required for adsorbing the same amount of Victoria blue having a molecular weight of 505.

A. Bencke [4] found that 1 gram of kaolin adsorbed 0·0038 to 0·0169 gram copper oxides from 50 c.c. of a solution containing 2 grams of copper sulphate ; it adsorbed 0·077 gram of ammonia from ammonium chloride, 0·373 gram barium from barium chloride, and 0·075 gram aluminium from aluminium sulphate from $\frac{1}{10}$ N solutions in three days.

[1] *Chem. Zeit.*, **47**, 115 (1923).
[2] *J. Amer. Chem. Soc.*, **44**, 523 (1922).
[3] *Landw. Vers. Sta.*, 1914, p. 85.
[4] *Sprechsaal*, **53**, 490–491 (1920).

If a typical plastic clay is shaken up with a solution of any one of various salts and the clay is then washed, it will be found quite impossible to recover all the salt added. This is due to the fact that it has been adsorbed by the clay particles and it can only be removed by adding another electrolyte which will displace the first one (see also *Flocculation* and *Deflocculation*).

It has been shown by C. F. Binns [1] that kaolins contain alkali which is not present as felspar or mica and is probably adsorbed in the free state; this is also confirmed by R. F. Geller and D. R. Caldwell's [2] discovery that several American kaolins adsorb 0·1–0·25 per cent. of sodium hydroxide.

The distribution of an adsorbed salt may be represented as shown in p. 236.

The presence of certain salts adversely affects the adsorption of others, the effect of sulphates being particularly noticeable in this respect. If, however, the sulphates are previously rendered insoluble by the addition of barium chloride, the resultant barium sulphate is quite inert. This is important in connection with the use of certain clays for casting and in the purification of other clays by means of very small proportions of alkalies or other electrolytes.

Clay not only removes salts as a whole from their solutions by adsorption, but it can adsorb either the base or acid ion (according to circumstances) from a dilute solution of a salt. Thus, when a liquid mixture of clay and water is filtered, the filtrate appears to be quite neutral to such an indicator as litmus or phenol-phthalein, but if a mixture of clay and a solution of salt (sodium chloride) is similarly treated, the clear filtrate will be acid to these indicators. The reason is that the salt in solution decomposes into its constituent acid and basic ions, and when such a solution is brought into contact with clay the clay adsorbs the base, which is thereby removed from solution, leaving free acid ions in the solution. Similarly, if a faintly alkaline solution of phenolphthalein or litmus is mixed with clay, the filtered liquid will be acid. Under favourable conditions, clay will remove about $1\frac{1}{2}$ per cent. of its weight of lime from a solution of lime in intimate contact with it. The apparently acid nature of china clay is not due to the clay being truly acid—as might, at first, be supposed—but to its removing the base from its combination with the indicator. A piece of neutral litmus paper left for some time in contact with moist clay will turn red for the same reason. On the other hand, clay will remove acid from a dilute solution by a similar process of adsorption, though to a much smaller extent than it will remove alkalies or bases.

Hence, if clay is kept in contact with a base or acid in solution it will remove some, or possibly all, of it by adsorption, the amount so removed depending on the physical condition of the clay and the form in which the base or acid is presented. Clay can be shown to be either acid or alkaline to indicators, according to the manner in which the test is conducted. Actually, its reaction does not depend on its being either acid or alkaline, but upon its power to remove soluble substances by physical or possibly physico-chemical processes of adsorption.

A phenomenon of greater interest with regard to clays brought into contact with

[1] *Trans. Amer. Cer. Soc.*, **8**, 206 (1906).
[2] *J. Amer. Cer. Soc.*, **4**, 468 (1922).

saline solutions is the power of the clay to adsorb some of the salt as a whole, so that when the clay is withdrawn from the solution and dried slowly some of the salt crystallises on its surface, causing what is technically known as "scum." The salts so removed are chiefly sodium, potassium, and calcium sulphates. They form only a very small proportion of the total weight of the dried clay, but as they are largely concentrated on the exterior of the mass they are readily noticeable, especially if the clay is dark in colour. This formation of "scum" is not wholly a colloidal phenomenon, as it can be produced by any aggregation of pores and with care can be formed from a bunch of capillary tubes made of glass.

I. M. Kolthoff [1] regards the adsorption of ions by solids to be a purely chemical phenomenon, in which one ion of a slightly soluble salt is replaced by another ion of a difficultly soluble salt, and is analogous to the exchange of bases which occurs in permutites.

The adsorption by clays is much more complex than in many colloids, as chemical reactions may occur between the granular matter and the adsorbed substances, as well as between the latter and the colloids. For instance, when acid or neutral salts are adsorbed, sodium, potassium, calcium, and magnesium from the clay may be released or dissolved, whilst an equivalent amount of the adsorbed basic radicle remains with the clay.

The reactions in the presence of alkaline solutions are still more complex. Free alkalies and basic solutions may be formed by the hydrolysis of salts of a strong base and a weak acid, *e.g.* carbonates and phosphates. Three different reactions are possible :—

1. The free alkali may react with colloidal silica.
2. The silicate radicle from the clay may form insoluble salts with an adsorbed base.
3. The sodium, potassium, calcium, or magnesium displaced from the clay may form soluble phosphates and carbonates, and these salts may be adsorbed by the clay.

It has been claimed that lime neutralises the acids in clay and also renders the potassium and sodium salts soluble.

Electrical Properties.—Several properties of clays are due to the fine particles bearing a negative *electric charge* ; thus, clay particles possess the properties of an electro-negative colloid and, when in suspension, they can effect the precipitation of electro-positive particles or ions as described on p. 230.

Brownian Movement.—The Brownian movement may be observed in many clay suspensions, though only a very small proportion of the particles in most clays are sufficiently fine to show it clearly. In ball and china clays, the proportion of particles which show the Brownian movement is much larger.

Alexander [2] found the Brownian movement in English china clay to be very active, but comparatively slow in American kaolins, except in the case of Florida kaolin and Laclede-Christy bond clay 69B, in which it is nearly as active as in English china clay.

Action of Electrolytes on Clay.—When various soluble substances are introduced into a slip or suspension of clay in water, they have the effect of flocculating

[1] *Koll. Zeit.*, **30**, 35–44 (1922). [2] *J. Amer. Cer. Soc.*, **3**, 612 (1920).

or deflocculating the clay in the same manner as colloidal sols and gels are respectively flocculated and deflocculated.

Electrolytes are of five categories :—

1. Acids, which cause flocculation of clays and electro-negative colloids.

2. Bases, which cause deflocculation of clays and electro-negative colloids.

3. Salts, which dissociate into acid and basic ions and may cause either flocculation or deflocculation.

4. Amphoteric electrolytes, which may cause either flocculation or deflocculation, according to circumstances, as aluminium and tin hydrates, which are soluble in both acids and alkalies.

5. Pseudo-acids and pseudo-bases, which are neither acids nor bases, but can become so by intramolecular rearrangement. Pseudo-acids and bases are neutralised very slowly on account of the time taken for the intramolecular rearrangement.

The effect of electrolytes upon a material also depends on the physical form of the latter ; thus, sodium carbonate has only a very feeble dispersive action on slate, a rather stronger action on shale, a much stronger one on fireclay, and most plastic clays and kaolins are readily deflocculated by a sufficiently strong solution of this salt.

Flocculation.—The phenomena of flocculation or precipitation of colloids have been described on p. 230 ; the flocculation of clays is similar. Clays may be precipitated or flocculated either (*a*) by colloids of opposite electric sign, or (*b*) by electrolytes.

Flocculation by Colloids.—If the colloidal sols of clay and iron hydroxide are mixed, a precipitate is formed which produces a red burning clay, from which the iron compound cannot be separated without destroying the physical properties of the gel.

The hydrosols of silica and alumina also precipitate each other. J. Splichal [1] found that the most rapid precipitation takes place when the ratio of alumina to silica is 1 : 3. Such a product would appear to bear a surplus electro-negative charge and confirms Purdy's [2] contention that clay particles are not neutral, but electro-negative, both in the flocculated and deflocculated states, as shown by the fact that they always migrate to the positive pole in the presence of an electric current, *e.g.* in kataphoresis and electro-osmosis.

Flocculation by Electrolytes.—Sven Oden [3] considers that when particles of clay are coagulated by the action of an electrolyte, they simply come together and adhere and so settle out of suspension, but otherwise preserve their individuality. This probably explains the fact that on shaking such a coagulated deposit sufficiently the particles are again dispersed, but if they are allowed to stand they recoagulate. If, however, ' the particles come into contact so violently that the film over them is destroyed,' the re-dispersion without the aid of a deflocculating agent is impossible. He also considers that the speed of coagulation is proportional to the size of the particles and the electric charges they bear.

[1] *Chem. Liste*, **15**, 53–56, 88–90, 110–113, 140–143, 164–167 (1921).
[2] *J. Amer. Cer. Soc.*, **5**, 477 (1922).
[3] *J. Landwirtschaft*, **3**, 177 (1919).

The flocculation of clay may be effected by any of the following agents :—

(*a*) An acid having an easily adsorbed ion of the opposite electric sign to the clay. Almost any acid may be used for this purpose, but the desirability of avoiding certain ones if the clay is to be used later for chemical purposes must be considered.

(*b*) An acid salt corresponding to (*a*) but possessing some minor advantage, either as regards cost or with respect to the future use of the clay.

(*c*) A salt having the necessarily easily adsorbed ions, such as alum, which is often used on account of its cheapness and convenience rather than because it is any better than either of the foregoing classes of precipitant. In some cases, the use of alum is advantageous, because, when decomposed with formation of aluminium hydroxide, it produces a very voluminous precipitate which readily enmeshes fine particles of sewage, etc. In this way, alum acts as a good clarifying agent.

(*d*) A colloid of opposite sign to the clay, *e.g.* ferric hydroxide or aluminium hydroxide. These are usually costly and so are only used where it is desired to precipitate the clay in the form in which the added colloid will be of use. If it is desired to increase the alumina content of a clay-gel, alumina or an equivalent aluminium salt may be used.

(*e*) An electric current may be used to decompose any salt and to liberate readily adsorbed positive ions which will then produce the desired flocculation.

N. M. Comber,[1] who considers clay particles consist of a central core surrounded by an emulsoid protective layer, suggests that coagulation may occur in three ways :—

Normal flocculation, as by salts of iron and aluminium, is the same as the coagulation of any electro-negative suspensoid by an electrolyte.

Indirect flocculation resulting from the interaction of the flocculant and the clay, normal flocculants being produced. Some neutral salts and acids are of this type.

Abnormal flocculation, due to a reaction of the emulsoid layer and the flocculant, as lime, which forms a direct precipitate. The flocculation of clay by lime is abnormal, as electro-negative suspensoids are usually deflocculated by alkalies. This abnormal behaviour is due, according to N. M. Comber, to the lime precipitating the emulsoid film surrounding each plastic particle, the precipitate being very voluminous, as with tannins, silicic acid, and humus. The precipitate entangles the cores of the clay particles, causing the suspensoid to settle rapidly and form a bulky deposit. If the hydroxyl ions are added before the calcium ones, the former deflocculate the clay and the lime afterwards produces a larger precipitate. If the hydroxyl ions are added simultaneously with the calcium ions, the former merely produce the alkalinity necessary for the reaction between the calcium salts and clay.

The following substances, according to Mellor, Green and Baugh,[2] coagulate clay slips and increase their viscosity ; grape sugar, humic acid, borax, ammonium chloride, calcium chloride, calcium sulphate, ammonium urate, aniline, ethylamine, methylamine. Greater or less concentration than those used in their tests may have a different effect. The following substances when added in small proportions to suspensions of clay cause flocculation and increase the viscosity : copper sulphate, dilute ammonia, potassium aluminium sulphate.

[1] *J. Agric. Sci.*, **11**, 450–471 (1921). [2] *Trans. Eng. Cer. Soc.*, **6**, 161 (1906–1907).

Ashley found the following also flocculate clays: ammonium nitrate, sodium sulphate, ammonium sulphate, magnesium sulphate, ferrous and ferric sulphates, lead acetate, carbonic acid, potassium dichromate, sodium acetate, hydrochloric acid, sodium chloride, zinc chloride, magnesium chloride, barium chloride.

Some substances which, in small proportions, cause flocculation will, when added in larger proportions, cause a reverse action (see p. 231). It is, therefore, necessary to ascertain the concentration at which the substance must be employed to secure the desired result.

It is commonly supposed that the flocculating power of any salt is proportional to its amount up to a certain limit, at which the material is so completely flocculated that no further addition of salt has any effect; conversely, the flocculating power of a given amount of salt is inversely proportional to the quantity of clay suspended in the liquid. The flocculating power of a salt also varies with both its acid and the metal ions. Table XCIX, due to A. D. Hall,[1] shows approximately their comparative effect:—

TABLE XCIX.—*Flocculating Power of Electrolytes*

Electrolyte.	Flocculating Power.	Electrolyte.	Flocculating Power.
Hydrochloric acid	30	Potassium nitrate	2
Calcium chloride	15	Sodium nitrate	1
Potassium chloride	3	Sulphuric acid	20
Sodium chloride	1	Calcium sulphate	5
Nitric acid	28	Potassium sulphate	1
Calcium nitrate	10	Sodium sulphate	0·5

Hardy,[2] however, has shown that the effect of an electrolyte is determined by its valency, trivalent kations being more efficient than divalent ones and divalent kations more than monovalent ones. Arrhenius [3] found that sulphuric acid, which is stoichiometrically twice as powerful as phosphoric, hydrochloric, and oxalic acids, effected the flocculation at twice the speed of these acids.

N. M. Comber [4] has found that clay is more readily flocculated from an alkaline suspension than from a neutral one and in this respect it resembles the emulsoid colloids such as silicic acid. He suggests that the particles of colloidal clay in a soil are protected and, therefore, act like an emulsoid coating to the larger grains of inert material and not like a suspensoid.

[1] *The Soil*, 39–40.
[2] *Proc. Roy. Soc.*, **66**, 95–109 (1899).
[3] *J. Amer. Chem. Soc.*, **44**, 523 (1922).
[4] *J. Agric. Sci.*, **10**, 425–36 (1920).

If a colloidal sol is of complex composition it may be fractionally precipitated by carefully adjusted quantities of the precipitating agent, and by this means one of the colloids present may be separated before the others. Thus, with very careful additions of acid, the greater part of the clay may be precipitated from a mixture of clay and silica sols and a more desirable product thereby obtained. Fractional precipitation is well known in ordinary chemical operations and its use in connection with sols involves no novelty but its practical importance is seldom realised.

The nature of the gel or precipitate is greatly affected by the concentration of the sol from which it is produced, by the temperature, the rate at which the precipitate is added, and even by the quantity of sol used at a time. Consequently, all these factors require careful attention in the preparation of a colloidal gel. It is also obvious that if a sol contains any other substances in suspension—such as minute flakes of mica which are enmeshed in the clay sol—these will be carried down into the clay gel unless they are removed by a process of fractional precipitation.

Flocculation increases the plasticity of clay pastes, which contain sufficient colloidal material, and it is one of the means employed for increasing this quality where it is lacking. Its action in this respect is limited by the amount of colloidal matter present (see p. 271).

Deflocculation.—One of the characteristic properties of a freshly precipitated clay—which may be regarded as a clay gel—is that it can be deflocculated, *i.e.* the particles are reconverted into a form in which they will remain indefinitely in suspension by the addition of a suitable electrolyte. This process is also termed peptisation (see also p. 235). Several theories as to the cause and procedure of deflocculation or peptisation of clays have been propounded by various investigators. Rohland considers it to be due to the addition of hydroxyl (OH) ions to the clay and states that they may be added in the form of any hydroxide, any salt containing a strong base and a weak acid, or any other suitable basic material of either organic or inorganic nature.

Later investigations seem to suggest that the principal cause of deflocculation is the adsorption of metallic ions. Freundlich attributes deflocculation to a lowering of the surface tension as a result of the adsorption of the added ions. If this is correct, the deflocculation of clay by very dilute solutions of sodium silicate or other sodium salts is due to the adsorption of the sodium ion by the mass of clay, the surface tension of which is then reduced sufficiently for the particles to escape and to be distributed through the liquid by the violent stirring which is usually an essential accompaniment of deflocculation.

Purdy regards flocculation and deflocculation as due to the difference in surface tension of the water in excess of the amount required to develop plasticity and the surface tension of the water-film, flocculation occurring when the surface tension of the water-film is less than that of the excess water and deflocculation when the surface tension of the water-film is greater than that of the excess water.

Another suggested explanation is based on the fact that, although it is generally considered that clay is neither soluble in water nor is it a solvent for water, yet, if an alkali is added either to the clay or to the water, some of the clay becomes " soluble."

In the case of complex acids, it is usual to explain that a neutral " salt " is formed which is soluble, and it is probably correct to say that the same occurs with clay, the product in this instance being not only more soluble in water, but a better solvent for water than the original clay.

There is clearly a great difference between the properties of a system of water dissolved in clay and of clay dissolved in water, and it is this difference which is usually overlooked.

The reason that some substances peptise clay whilst others coagulate it, appears —at least in some cases—to be due to the fact that, in the first case, the compound of clay and added substance is sufficiently soluble for the whole system to turn in the direction of a more mobile solution, whilst in the latter case, the compounds produced are less soluble in water, have a lower hydration capacity, and so are more easily separated (by coagulation) from the dispersion medium.

Many substances will lower the surface tension of the mass of clay and serve as deflocculating agents, so that it is possible to use—

(i) A liquid such as water. Water is so readily decomposed (hydrolised) into what may be regarded as acid- and basic (OH) ions that it acts as a powerful deflocculating agent, though its action is greatly increased by the addition of a little acid or alkali as may be required. In deflocculating clay, a little alkali (such as ammonia, soda, etc.) is used, as acids have an effect on clay which is the opposite to that of deflocculation. Heating the water aids the deflocculation, and for this reason hot water is sometimes used in pottery-mixing machines or blungers so as to secure the more rapid production of a uniform slip.

(ii) A non-electrolyte, such as many organic liquids (they are too costly).

(iii) An ion such as is produced by the dilution of some solutions of salts and other soluble substances, two groups of ions being formed, one of which can be adsorbed by the clay. Sodium carbonate, for example, splits up when in a sufficiently dilute solution into sodium ions and CO_3 ions ; the sodium ions are at once adsorbed by the clay, whose surface tension is thereby lowered, thus liberating the particles of clay ready for dispersion by the mechanical process of stirring or by the slower process of diffusion. The oxides and hydroxides of calcium, barium, sodium, or potassium are very satisfactory deflocculating agents, the last two being very powerful. M. Simonis [1] has found that lithia is even more powerful than soda in increasing the suspensibility of clays, and soda is, in turn, more powerful than potash. Other substances which act in a similar manner include various soluble phosphates, carbonates, and silicates. Some substances, such as borax, act in the reverse direction to what is anticipated, and cause flocculation instead of deflocculation. Mellor, Green and Baugh [2] found that the following substances increase the fluidity of clay slips when small proportions of them are used ; but with larger proportions, the fluid becomes more viscous : sodium carbonate, potassium carbonate, " fusion mixture," potassium sulphate, potassium bisulphate, potassium hydroxide, potassium nitrate, sodium sulphide. The following substances also cause deflocculation, though some of them, when at a greater or less concentration than those used by these investigators, may

[1] *Sprechsaal*, 39, 1167, 1184 (1906).

[2] *Loc. cit.*, p. 244.

have a different effect: sulphates of magnesium, mercury and sodium, sodium sulphide, acetate, chloride, phosphate and silicate and ammonium gallate.

Ashley has stated that the following alkali-salts also deflocculate clay: sodium oxalate, potassium oxalate, ammonium oxalate, soft soap, borax, potassium phosphate, disodium-hydrogen phosphate, sodium dihydrogen phosphate, sodium-hydrogen-ammonium phosphate, potassium cyanide, potassium ferricyanide, sodium arsenite, potassium permanganate and many dyes.

If the ions which take no part in flocculating or deflocculating the clay can combine with any other substance which is present, they may form an insoluble compound which is then precipitated. Thus, on adding sodium carbonate to a clay gel containing lime, the sodium ions effect deflocculation, whilst the CO_3 ions combine with the lime and form insoluble calcium carbonate which is precipitated.

(iv) A salt which is decomposed into its constituent ions, as just described.

(v) A deflocculated colloid, the particles of which bear the same electric charge as the clay or other substance to be dispersed.

(vi) A mixture of two or more deflocculating agents, such as a mixture of sodium carbonate and silicate (water-glass).

(vii) The removal of an agglomerating agent, if present, from a colloidal substance will often effect its deflocculation and conversion into a sol. Thus, some clays which contain humus derived from decomposed vegetable matter, produce sols of an entirely different character if the humus is destroyed by sulphuric acid or ammonia, or if it is removed by washing the clay with water. This process is of very limited application.

In the case of materials which are not pure, it is sometimes necessary to convert any interfering impurities into an insoluble or inert form before commencing the deflocculation; thus, any soluble sulphates present should be precipitated by the addition of barium hydroxide prior to adding the deflocculating agent. The barium hydroxide serves a double purpose, first, rendering the sulphates harmless, and any surplus deflocculating part of the clay.

It is most important in deflocculating clays that exactly the right proportion of alkali or other agent should be added, as when too much or too little is used a reverse action may take place. The permissible range is often very small and, in the case of some clay slips examined by H. Kohl, the minimum viscosity was obtained with 0·3 per cent. of sodium carbonate and the maximum viscosity with 0·83 per cent. With another fine clay, A. Mayer found that the maximum amount of electrolytes which would allow 100 grams of the clay to remain in suspension in 500 c.c. of water were as follows: 2·5 per cent. of ammonia and 0·025 per cent. of each of the following: sulphuric acid, hydrochloric acid, nitric acid, alkali sulphates, chlorides, or nitrates.

Purdy explains the changes which result from the action of electrolytes by suggesting that when an alkali is added and is adsorbed by the water-film (p. 246), the surface tension is increased and deflocculation occurs. When a maximum has been added the remainder goes into the excess water, increasing its surface tension so that flocculation occurs.

The effects of alkalies on clays are sometimes further complicated by three or four

colloid-chemical processes overlapping each other. Wo. Ostwald has summarised them as follows :—

(*a*) The clay, an electro-negative colloid, is deflocculated by the addition of alkali. This puts it into a more highly dispersed state, an effect entirely similar to that observed when other negative colloids (like the metals) are treated in this manner.

(*b*) A swelling is produced and attains its optimum at a slightly higher concentration of alkali than that needed for deflocculation. Time is needed for this swelling.

(*c*) Alkali attacks the organic colloids (humus, etc.), deflocculating them with small amounts of alkali, but larger amounts leach them out and bring them into a molecularly dispersed condition. In this way, they lose their importance as " protective hydrated emulsoids."

(*d*) In time, the deflocculation and the increase in viscosity tend to nullify each other.

Deflocculation reduces the plasticity of clays, whilst flocculation increases it. Consequently, it is possible to decrease the plasticity of an almost dry clay by mixing it with a small quantity of a very dilute solution of alkali instead of plain water.

Protection of Clay Suspensions.—For the reasons given on p. 232, a clay-suspension may not be precipitated on the addition of a coagulant if a protective colloid is also present. To some extent, plastic clays also act as protective colloids, because they effect the suspension of non-colloidal and non-plastic particles. Even when a protective colloid cannot completely prevent flocculation, it may greatly increase the minimum amount of electrolyte necessary to produce flocculation. When flocculation occurs, the protective colloid also aids in preserving the resulting gel-structure, so that deflocculation is more readily effected than when no protective colloid is present. Thus, in the case of a gold colloidal sol, a small proportion of tannin is used as a protective agent. The sol may be evaporated to dryness, kept indefinitely, and when required for use it is simply dropped into water and is thus restored to its original sol state. In the case of clay slips, the valuable protective powers of the humus compounds in the soil and in decomposed urine have long been recognised in an unscientific and empirical manner. Still more recently, J. P. Guy has found that the addition of a little specially prepared sewage sludge to fireclay used in making saggers adds greatly to their strength. This is attributable to its protective action on the colloids in the clay.

The presence of certain adsorbed salts appears to be necessary for the stability of clay suspensions ; this is also a characteristic of many colloids (p. 238). B. Moore and others hold that when the last traces of electrolytes are removed from colloidal sols, the latter are denatured or polymerised with resultant coagulation, and they maintain that small quantities of such electrolytes are essential to the stability of the colloid sol state. The higher alkali content of ball clays may possibly account for their greater colloidal properties as compared with those of china clays.

Kataphoresis.—Like colloidal sols (p. 229), clays are influenced by an electric current, the clay particles behaving as an electro-negative colloid and travelling towards the positive pole or anode. This property is used in the drying of clay-suspensions by electro-osmosis, and B. J. Allen has used the phenomenon of kata-

phoresis to effect the deposition of clay or mixtures of clay and non-plastic materials in the method of moulding ware by the casting process. Use may also be made of kataphoresis to prevent clay from adhering to metal discs and to the mouthpiece of extrusion or "wire-cut" brick machines, as it has been found that if an electric current is passed through the clay paste and metal, the latter forming the cathode, the clay is repelled from the metallic surface, whilst some of the water in the clay is attracted to it and forms a film of water between the clay and the metal by which efficient lubrication is effected.

Miscibility.—Two plastic clays cannot always be mixed to form a homogeneous paste, probably for the same reason which makes it impossible for one colloidal gel to take up water from another, so that if one contains more water than the other a state of equilibrium cannot be obtained and the moisture remains unevenly distributed in the mass. The only clays which can be mixed in the wet plastic state are those containing small amounts of colloidal matter, and this should be as far as possible in a deflocculated condition.

It is a very peculiar fact that if two clay pastes are made, one with water and the other with an oil, and are mixed together, the plasticity is entirely destroyed. This appears to be a colloidal phenomenon, though it has not been fully explained.

Semi-permeability.—According to Rohland, plastic clays will allow ferric chloride and sugar (solutions) to diffuse through them, but not tannin (colloid). In emulsions of oil and water, plastic clays permit the (solution) water to pass, but not the (colloid) oil. In alcoholic solutions of fat, such clays permit the alcohol to pass, but not the fat. In aqueous rubber solutions, plastic clays prevent the rubber from diffusing, and in albumen solutions the albumen is retained, both rubber and albumen being typical colloids. The diffusibility, or speed at which the substances dialyse through the membrane, depends on their nature. Thus, water, which is a solution, and electrolytes, *e.g.* salts, dissolved in it, diffuse rapidly, but colloids, such as ferric hydroxide, hydrated silica, hydrated alumina, and most products of organic life, such as starch, vegetable oils, and gelatin, are either indiffusible or pass through with extreme slowness. Colours, on account of their complex composition, play a special part; they are retained by plastic clays, though these colours are solutions and not colloids. Berlin blue, potassium ferricyanide, aniline blue, sulphated triphenyl, rosaniline, aniline red, carmine, malachite green, fluorescin, aurin, and other animal, vegetable, and tar colours, cannot diffuse through clay, and this in spite of the fact that they are true solutions.

The explanation of semi-permeable membranes most widely accepted at the present time is that of selective solubility, suggested by L'Hermite. The membrane is permeable to those substances which dissolve in it, but not to others.

As the semi-permeability of clays appear to be connected with the plasticity, any treatment which will increase the latter should increase the former. Rohland has found this to be the case with some lean clays he has examined. Some of the phenomena occur whenever plastic clay is mixed with solutions, as the particles of clay allow these to pass through them, but retain any colloids on their surface. In this way the adsorption of dissolved as well as colloidal matter occurs, but as

the particles of clay are so minute, the effects are scarcely distinguishable and clays appear to be capable of absorbing both colloidal and dissolved substances.

Measuring Colloidal Matter in Clay.—It is extremely difficult to estimate the proportion of colloidal matter in clay and other ceramic materials, because of the difficulty of separating it completely. A large part of the non-colloidal matter may be separated by making the clay or other material into a slip with water, but the separation is far from complete and much of the colloidal matter may (and probably does) adhere to the grains of non-colloidal matter and cannot be separated from them. Attempts to separate the colloidal matter by means of a solution of sodium carbonate give such low results as to make it appear improbable that they separate more than a small proportion of colloidal matter. There is no sound reason for supposing that colloidal clay is soluble in sodium carbonate solution, and the use of this reagent is probably based on its dispersive power and on the fact that finely-divided silica is dissolved by it, rather than on any intrinsic relationship with the solubility of colloidal clay. If colloidal clay is not appreciably soluble in sodium carbonate, the low results obtained with highly plastic clays is at once explained.

Dialysis — which is excellent for separating colloidal matter from dissolved substances—is useless for separating it from insoluble matter.

Among the indirect methods of estimating the colloidal content of clays may be mentioned the use of aniline dyes, particularly malachite green, which is readily removed from solution by plastic clay. Ashley's method of estimating the colloidal content by means of this dye is described on p. 240. Unfortunately, the results must be referred to a " standard clay," as they cannot, at present, be obtained in absolute units. The difficulty of determining the proportion of colloidal matter in a plastic clay is still further increased by the fact that if the residue from which the colloidal matter has presumably been separated be agitated sufficiently, a further quantity of colloidal matter may be separated, this proceeding until the residual grains are so hard that they cannot readily be converted into the colloidal state. Thus, if a fine clay is subjected to a sufficiently intensive crushing and dispersive action in a Plauson mill or similar device, almost the whole of the true clay can be converted into the colloidal state.

Much further research is needed before a satisfactory method of determining the colloidal content of clays is found (see also p. 263).

Other Colloidal Materials used in Ceramics

Apart from clays, few materials possessing active colloidal properties are used to any great extent in the ceramic industries.

Active Colloids.—The most important active colloids are :—

Colloidal alumina, which is present to a small extent in bauxite and laterite, can also be prepared artificially, but is much too costly to be used on a large scale. Colloidal alumina is presumed to be produced when aluminium nitrate is rendered slightly acid with nitric acid. This method of manufacture, and the use of the product as a bond for bauxite bricks, was patented by E. Podszus in 1912.

Colloidal silica occurs to a small extent in an active form in nature, and can be made artificially by carefully mixing hydrochloric acid and water-glass and removing the resultant salt by dialysis. The use of colloidal silica as a bond for silica bricks was patented by C. V. Boys in 1889, by A. Poulson in 1909, by Schwerin in 1912, and by A. Schlossberg in 1913. Its use as a bond for magnesia bricks has never passed the experimental stage.

Colloidal silica, when suspended in water, behaves much more like an emulsoid—in which the suspended particles appear to be in the form of minute drops—than a suspensoid—in which they appear to be minute solid particles. For example, the electrical properties of colloidal silica and the effect of electrolytes are rather obscure. A small amount of acid increases the stability of the silica sol, which is electrically neutral with low concentrations of H ions, positively charged with a high H concentration and negative when containing OH. The maximum stability of the sol at the iso-electric point is characteristic of emulsoids, but in sharp contrast to suspensoid sols. The effect of neutral salts on silica sol is also characteristic of emulsoid sols.

Silicic acid is the only rigid gel which has been studied exhaustively. It is prepared by adding a small quantity of ammonia to a carefully dialysed silica sol. If the gel is dilute, it retains its solidity, but from concentrated gels containing 5 per cent. or more of silica, water gradually separates—this segregation being known as " syneresis."

Pure silica gel, if left in air, rapidly dries to a transparent glass, which still retains several molecules of water removable at atmospheric temperatures by drying over sulphuric acid. There appear to be no definite hydrates, but a continuous loss of water with an equilibrium corresponding to every vapour pressure, and in this respect the gel differs radically from crystals with water of crystallisation.

The process of drying is reversible in parts, but rehydration shows a delay known as " hysteresis."

The dried gel, when placed in water, disintegrates, but it will absorb organic liquids without cracking. The structure of the gel appears to be porous, the pores being about 3 $\mu\mu$ diameter.

Examination of the fresh gel by X-rays does not show any crystalline structure, but this is observable in the dry, and particularly in the ignited, gel.

Silica gel has valuable adsorbent properties, and its use for adsorbing ether, benzene, acetone, alcohol, gases, etc., is steadily increasing.

Quartz sand, though showing no obvious optical colloidal properties, frequently behaves like a colloid. If, for instance, a dialysed sol of ferric hydroxide is passed through a column of carefully purified and ignited quartz sand, the ferric hydroxide is completely retained and only clear water leaves the column until all the colloidal silica has been used up.

The effect is due to the ferric hydroxide being a positively charged sol, whilst quartz in contact with water is charged negatively. This is borne out by the fact that acid sols of ferric hydroxide which have a negative charge pass through the column unchanged.

Colloidal magnesia has been patented by E. Podszus in 1912, and by B. Schwerin in the same year, as a bond for magnesia bricks.

Colloidal organic matter, such as humus (p. 232), linseed oil, fat, cellulose, lye, peat, gelatin, dextrin, gum, starch, etc., are largely used as temporary bonds in the manufacture of articles from non-plastic materials to enable them to form a sufficiently strong mass in the dry state and prior to the production of a fused bond in the kiln.

Irreversible Colloids.—Natural colloids other than clay, which are used in the ceramic industries, are chiefly found in the form of irreversible gels and possess no active colloidal properties, though they are quite clearly colloidal in character. Opal, geyserite, siliceous sinter, chalcedony, quartzine, lutecite and hyalite are of this nature, and it has been suggested that the colours of some opals and other precious stones are due to the mutual precipitation of two colloids of opposite sign, such as ferric hydroxide and silicon hydroxide (hydrated " silica "). In many sedimentary rocks, including some of those used as refractory materials, the grains of aggregate are united by irreversible gels of silica, ferric hydroxide, etc., though in some cases the cement has crystallised at a later stage in the history of the material. In most cases, the gel is dehydrated simply by the pressure of the superincumbent rocks. Gross [1] has suggested that some forms of graphite are probably the result of colloidal flocculation followed by the aggregation of the flocculated particles.

CHANGES DUE TO WATER IN NATURAL MINERALS

The changes in the physical state of clays and other ceramic materials due to the application of or removal of water in the ordinary course of nature are commonly regarded as the result of " weathering." They include the action of rain, snow, and frost in winter, and of sunshine and rain in summer—the former is sometimes known as " wintering " and the latter as " summering " or " sunning," but it is convenient to regard all under the term " weathering."

Physical Changes effected by Weathering

When clays and other raw materials used in the ceramic and allied industries are exposed for a sufficient time to the action of the weather, they may undergo one or more of the following changes :—

(*a*) Mechanical disintegration due to the freezing of water in the material.

(*b*) Physical changes which are dependent on the behaviour of water absorbed by the material.

(*c*) Chemical changes such as those described in Chapter XI.

Most fired ceramic materials are highly resistant to the action of the weather and for that reason many of them are of great value for building and constructional work.

The principal physical changes wrought in clay by exposure to the action of the weather are :—

(*a*) Moisture is absorbed up to the limit of the hygroscopicity of the clay.

[1] *Jahrb. Rad. Electr.*, **15**, 270 (1918).

(*b*) The moisture is more uniformly distributed.

(*c*) The cohesion of hard masses is decreased by the formation of water films which surround the individual particles.

(*d*) The plasticity (p. 257) is increased.

(*e*) Oxidation of some of the mineral and other constituents of the clay occurs whereby the physical character of the clay is altered, *e.g.* a very sticky clay may become easier to work. As some iron minerals change their colour on exposure they may be more easily recognised and picked out of the weathered clay. Pyrites, on the contrary, may break down and be more difficult to separate.

Absorption of Moisture.—Ceramic materials have the power of absorbing moisture from the atmosphere into their pores. If the weather becomes sufficiently cold the water is frozen, and as ice has a greater volume than the water from which it is produced, it exerts an enormous pressure on the ceramic material and may cause it to burst or disintegrate. Such an action is beneficial in the case of clays and some other materials, because it not only reduces the cost of crushing and grinding the materials, but it has the advantage over disintegrating machines, such as stone-breakers, crushing rolls, and grinding mills, in that the frost works from inside instead of externally from the surface of the material towards the centre and, consequently, produces effects which cannot be obtained in such machines. If sufficient time can be allowed, most materials used in the ceramic industries may be disintegrated by frosty weather, but the porous materials are most readily and rapidly disintegrated, as the water can more easily penetrate into the pores of the mass.

In addition to the disintegrating effect of water at the moment when it is converted into ice, water in its liquid state has a disruptive action on some materials, partly on account of its solvent action on the cementing or binding agent in the materials, and partly as a result of its direct mechanical action in penetrating between the grains. In both these cases, its action is so slow that many years are required for an appreciable action to take place in non-plastic materials, and for that reason there is little to be gained by exposing them to the weather for only a year or two. Where a non-plastic deposit which has been weathered for many years is available, its value is often much greater. In some non-plastic materials, a chemical change, such as the oxidation of impurities, may occur, but this is dealt with in Chapter XI. Clays differ from the materials just mentioned in being very sensitive to the action of absorbed water, as they are both hygroscopic and porous, whilst sand and silt are much less hygroscopic and only absorb a very small proportion of moisture from the atmosphere. When clay is left exposed to the atmosphere it absorbs up to 20 per cent. of its weight of water without appearing to be wet, and it is almost impossible to keep a fully dried clay perfectly dry, unless special precautions are taken to keep it out of all contact with moisture.

The absorption of water by clay is a very complex phenomenon, and one which has not yet been properly explained, though clay behaves in this respect like a colloidal gel (p. 237), and if, when in a dry state, it is brought into contact with water, it will absorb a large quantity and will swell like glue without losing its solid character.

Rohland has suggested that clays continue to absorb water until the colloidal matter in them has gathered sufficient water to dissolve or render active all the dormant material present. When this has taken place, and the smaller grains are fully saturated, no further absorption occurs and any additional water will tend to produce a less cohesive mass as the film between the grains becomes thicker. Finally, if sufficient water is added, a slip or suspension will be produced in which the finer particles of clay will remain in suspension for an indefinitely long time. According to Sven Oden,[1] the amount of water held hygroscopically by clays depends upon their coarseness, fine-grained clays holding more water than coarse-grained ones. The hygroscopicity varies with the vapour pressure of the air surrounding the material. The power possessed by a clay of absorbing water also depends on the capillary pores in the clay, though it is not proportional to the actual porosity, as the large pores do not hold so large a quantity of water by capillary attraction in relation to their volume as the small pores. The absorptive power of clays is modified by their density, which, to some extent, prevents them from readily absorbing moisture and also from parting with it readily. When a piece of dry clay is immersed in water, the penetration of the latter causes a partial breakdown of the clay on account of the water entering into the pores of the clay and softening and separating the particles. This breaking down is termed " slaking " (see p. 257). When water is absorbed by clay there is a very slight and practically negligible rise in the temperature of the material. This is a property of colloidal gels (p. 235).

Distribution of Moisture.—The water in raw clays is seldom uniformly distributed, and it requires a considerable amount of time before uniformity can be secured, especially with highly plastic clays, such as ball clays. For this reason, it is customary to allow clays to be exposed to the weather for several months, and in some instances for several years, before using them.

The time taken to properly weather different materials varies greatly according to their nature. Thus, a comparatively soft clay may merely require to remain exposed to the weather for a few days or weeks. Other materials, such as hard shales, require two years or even more. Many shales used for making bricks are exposed for at least a year and a half before using, whilst Stourbridge clays are weathered for two or three years.

Some clays are very peculiarly affected by weathering ; thus, some of the Durham clays—especially those from the Five Quarter and Bottom Busty seams—become less plastic the longer they are exposed. Some of the clays used for making tiles in the Midland counties are adversely affected by weathering in wet weather. Where possible, the clay should be dry before it is exposed to the weather, as it is then in a more permeable state. Clay which has been wetted on the surface may be quite impermeable to water and, therefore, unaffected by rain. The best conditions are obtained when a dry clay is immersed in water and thereby thoroughly saturated prior to exposure to the weather. Such a procedure is seldom practicable, so that the best method generally available is to spread it out in comparatively thin layers and expose it directly to the action of rain, frost, and snow. If the exposure is

[1] *Trans. Faraday Soc.*, **17**, 244 (1922).

continued during fine weather any excess of moisture will gradually be removed by the atmosphere, the clay only retaining sufficient water to saturate it hygroscopically.

Disintegration.—The disruptive effect of frost and the softening action of absorbed water will together reduce the cohesion of a clay to such an extent that most clays, after weathering, will mix much more readily with water when treated in the ordinary mills and mixing machines, and will, consequently, produce a more even and uniform paste than can be made from clays which have not been weathered.

Oxidation effects are largely the result of chemical action and are described on p. 254, and in Chapter XI.

Increase in Plasticity by Weathering (see p. 271).

Artificial Weathering.—It is sometimes desirable to increase the action which would take place during weathering and especially to increase its velocity. Such treatment may be regarded as artificial weathering. This includes such simple processes as " watering " the clay with a hose-pipe, turning the material over to expose fresh surfaces, drying the material by artificial heat prior to exposing it to the weather or in order to reduce excessive plasticity, etc.

When the action of cold water is not sufficiently intense, hot water or steam may be substituted.

Steaming has a similar effect on clay to exposing it to the action of weather. Its chief actions are to—

(*a*) Supply the water required by the colloids present in a form in which it can act more intensely than is possible with cold water.

(*b*) Secure the uniform distribution of moisture throughout the mass.

(*c*) Increase the temperature of the clay and so ensure a greater amount of fermentation of the organic matter present.

By these means, the plasticity and binding power of the materials are increased and the clay so treated is more easily shaped. When only a small amount of moisture is to be added to a clay it can be distributed more uniformly if applied in the form of steam. Some fireclays are much more readily disintegrated by steam or hot water than by cold water.

Influence of an Excess of Moisture in Raw Materials.—Where raw materials are to be ground before being made into a paste, it is desirable that they should be as dry as possible. This is especially the case with plastic clay which, when wet, forms a sticky mass which is very difficult to grind. When the articles to be made can rightly have a somewhat rough texture, fine grinding is not necessary, and plastic clay may be sufficiently crushed in rolls, or in an edge-runner mill with a solid pan, but where a fine texture is required, it is preferable for the clay to be dry before it is ground, the requisite amount of water being added later at a suitable stage in its preparation.

When it is necessary to mix two or more clays together, the presence of water renders the formation of a homogeneous mass much more difficult and sometimes impossible, whereas if the clays are dry they can readily be mixed together and water afterwards added so as to produce a uniform paste of the required consistency.

Instead of drying a wet or plastic clay, it is sometimes sufficient to add some

non-plastic material, such as grog or dry clay. The material so added absorbs some of the excess of water in the clay and produces a more easily workable material.

PHYSICAL CHANGES IN CLAY AND OTHER PASTES

The previous section has been largely confined to the effect of water naturally absorbed from the atmosphere by various ceramic materials. In order that such materials may be made uniform in texture and readily shaped, it is usually necessary to subject them to various processes, such as crushing, grinding and mixing, in the course of which more water is simultaneously added, so as eventually to produce a plastic paste. Some clays naturally contain a sufficient proportion of water and no addition is then required. The principal property which such pastes should possess is that of " plasticity," though other properties are often essential.

Slaking

When a " lump " of clay is immersed in a large volume of water it gradually softens and eventually falls to a soft " mushy " mass. This change is known as " *slaking* " ; it has an important practical significance, because those clays which slake most rapidly can be more easily tempered or mixed with water to produce a homogeneous paste.

The time required to slake a clay varies according to the porosity of the material and the cohesion of the particles. A soft, porous, lean clay may be completely slaked in a few minutes, whilst a highly plastic material may not be fully disintegrated after several weeks. The speed of slaking is increased if the water used to effect it is slightly alkaline.

Sokoloff determines the rate of slaking of a clay by mixing it with various proportions of sand, making these mixtures into small pyramids, which are thoroughly dried at 100° C. and then allowed to stand on a small wire grid immersed either in still or running water, until the mixtures have completely broken down. Running water is best for plastic clays, as it is difficult to see the end point in still waters on account of the turbidity of the liquid, whereas the running water removes the finest particles as the test-pieces fall.

Plasticity

Plasticity may be defined as that property of a material by means of which it may be deformed or changed in shape and yet retain that shape when the deforming force is removed. Plasticity is thus very similar to malleability in metals, though the force required to change the shape of a plastic material is far less than that required for a malleable one.

Many materials are plastic, but clays are almost unique in the fact that their plasticity is destroyed though their shape is retained by removing the water which appears to be essential to their plasticity. Some synthetic plastic materials are plastic when hot but rigid when cold, others are only plastic when under great pressure

and become rigid when the pressure is released. Others again—like rubber—are plastic when cold, but are hardened by heat if they contain sulphur or some " vulcanising " agent, but clay is almost unique in the extent of its plasticity combined with the fact that this property is destroyed merely by the removal of the water from the material. A plastic substance differs from a viscous liquid and from an elastic solid, because both these substances regain their original shape when the deforming force is removed. At the same time, the plastic state is really intermediate between the two extremes of solid and liquid, as plastic materials possess some of the properties of both solids and liquids. Thus, a plastic substance, under great pressure, flows like a viscous liquid, but when the pressure is removed it retains its shape like a solid. It has the appearance and general behaviour of a soft and extensile solid, yet directly sufficient pressure is applied its fluid properties predominate.

Plastic materials appear to be divisible into two groups :—

(*a*) **Homogeneous substances** which are plastic under certain conditions of temperature but not under others, *e.g.* glass, sulphur and many similar materials are plastic when partly melted. This plasticity appears to be analogous to the viscosity of liquids. Although experimental evidence is not available, it is possible that these apparently homogeneous substances may consist of solid and fluid phases.

(*b*) **Two-phase substances** which owe their plasticity to the simultaneous presence of solid particles and of a fluid which acts as a lubricant and also as a cement for the solid particles.

Plastic ceramic materials and putty (whiting and oil) belong to this group. Such substances are a combination of solid particles surrounded by films of fluid which form a viscous coating sufficiently thick to permit the particles to move relatively to each other when subjected to a pressure which is less in one direction than in others (*i.e.* a shearing force). Highly mobile liquids having a low viscosity cannot be used to produce a plastic substance, as the films would be insufficiently buoyant and adherent. Water is satisfactory as it has a moderate viscosity, though under some conditions more viscous fluids will give a greater plasticity. Thus, certain oils or glycerine may be used and have the advantage, for some purposes, that the plastic product containing them does not " dry." Sometimes oils are used instead of water by crucible makers, etc., to produce a very plastic mass.

Plasticity appears to be due to a very delicate balance between (*a*) a force tending to hold the material rigid, and (*b*) a force tending to make it flow readily. It may be compared to the phenomenon of lubrication in which the lubricant consists either of soft gelatinous material or of a fluid covering hard cores of non-plastic material. The maximum plasticity is obtained when each non-plastic particle is completely surrounded by a layer of such a thickness as will provide the greatest amount of lubrication consistent with the maintenance of shape after the removal of the deforming force. If the film is too thin the lubrication is not effective, whilst if it is too thick the particles do not remain stationary when the deforming force is removed. The varying amounts of " lubricant " necessary to give the maximum plasticity depend, in the case of clay, on the properties of the clay itself, especially as in this case the " lubricant " appears to be a highly viscous liquid, consisting of a colloidal suspension

of clay in water. In this respect plastic clay is almost unique, as it has a high plasticity which is due to a very large extent to the action of water on part of the clay.

It will readily be understood that the nature of both the lubricant and the lubricated grains is of great importance, because this determines the nature of the materials which, when added, will produce a plastic mass. If the grains of aggregate are largely inert (as sand), the added liquid must be highly viscous and adhesive as well as possessing the necessary lubricating power. If, on the contrary, a viscous liquid can be made by the action of water on part of the aggregate, water alone may develop the plasticity. Sometimes the addition of a suitable proportion of another substance, such as an acid, may, by altering the colloidal state of a material, greatly increase (or diminish) its plasticity.

Solid substances vary greatly in the material which must be added to produce a plastic mass. Most inert materials—especially if they consist of dense, impervious grains—are not capable of being "lubricated," and so made plastic in the manner mentioned above, whilst some substances are more capable of being "lubricated" than others. The ideal conditions of lubrication are obtained when highly porous, non-plastic, inert grains have such an intermolecular attraction for the lubricant as to retain a film of the desired thickness on their surfaces. This condition is met with in very few natural materials, the most important in the ceramic industries being certain clays which may be regarded as consisting of large molecules having an interatomic space-lattice structure, such as has been suggested by Bragg in his researches on the structure of crystals. This type of structure, containing, as it does, a relatively large proportion of combined water, will more readily retain the "lubricant" on its surface than will simpler molecules. Consequently, clay will develop a high plasticity with water, whilst so-called non-plastic materials show none except under conditions of extreme fineness when they become feebly plastic. When a suitable liquid, other than water, is used, some plasticity is developed as in the case of putty, which is made from whiting and oil, the latter acting as the "lubricant."

Omitting, for the present, those materials in which the plasticity is due to the use of oil or of added materials, other than water, the plasticity of clays has been attributed to—

(i) The size of the solid particles.

(ii) The shape of the solid particles and their internal structure.

(iii) The aggregation of the solid particles.

(iv) The surface area of the solid particles and intermolecular attraction.

(v) The effect of water on the solid particles and colloidal phenomena connected therewith.

(vi) The presence of other materials which may have an influence on the properties of the mass.

Plasticity is not directly connected with the chemical composition of the material, though where changes of composition do occur—as when clay is heated—the plasticity may be destroyed and cannot be restored in a simple manner. This is usually due to the decomposition of the material, whereby the size of the individual particles is altered and their other physical properties are affected. The finest clays are generally

less plastic than those containing a larger proportion of impurity. Thus, china clays and kaolins are the nearest approach to what is considered to be true clay and yet they are only slightly plastic. Many attempts have been made to correlate plasticity and composition, but hitherto without much success. This may be due to very minute proportions of some substances having a great power; thus, H. Spurrier [1] has found that the ratio of the alumina and silica dissolved from clays by caustic potash decreases with the decreasing plasticity of clays.

Effect of Size of the Particles.—Various investigators have attributed plasticity to the extreme smallness of the grains of a material, because various materials usually considered to be "non-plastic" may, when very finely ground with water, develop a small amount of plasticity. Quartz and limestone, when ground to pass a 200-mesh sieve and then mixed with a small proportion of water, have, according to Wheeler,[2] a slight plasticity, but do not hold together on drying. Orton [3] found a similar effect with ground glass, and Cohn and Atterberg found that precipitated barium sulphate and calcium fluoride are plastic when wetted. Wet-ground felspar, which has been allowed to stand for some time, has, according to Daubrée, a slight plasticity.

The plasticity developed by grinding non-plastic materials is, in all cases, so small that, whilst it must be admitted that the size of the particles certainly is in some way connected with plasticity, yet it is only one of the factors involved. That it ought not to be overlooked is shown by the fact that, if the fine particles of a plastic clay are all removed, the residue usually loses its plasticity.[4] On the other hand, the clays composed of the finest grains are not necessarily the most plastic and many materials consisting almost wholly of fine grains are not appreciably plastic. It is certain, however, that the size of the grains has some effect, as the plasticity of a material may often be increased by finer grinding, whilst the inclusion of coarser grains decreases the plasticity. At the same time, plasticity is not wholly due to the small size of the particles, because when a clay is decomposed by heat into silica and alumina the resulting particles should be smaller than the original grains, and, consequently, should be more plastic when wetted; yet this is not the case, as such particles are entirely non-plastic.

Effect of the Shape and Structure of the Particles.—The plasticity of clays has been attributed to their lamellar or platy nature by Johnson and Blake [5] and others, including Biedermann and Herzfield,[6] Cook,[7] Howarth,[8] Wheeler,[9] and Le Chatelier. Thus, Wheeler found that calcite, gypsum, talc and pyrophyllite, which consist of minute plates, develop some plasticity when wet, but have little strength when dry, and also that mica and glauconite, if ground sufficiently fine, produce pastes equally as plastic as clay, though mica requires very prolonged grinding, as the lamellæ are extremely elastic.

[1] *J. Amer. Cer. Soc.*, **4**, 113 (1921).
[2] *Mo. Geol. Survey*, **11**, 102 (1896).
[3] *Brick*, **14**, 216.
[4] Some clays from which the finest particles are removed do not appear to lose their plasticity (see p. 263).
[5] *Amer. J. Sci.*, **2**, 351 (1876).
[6] Bischof, *Die Feuerfesten Thone*, 23.
[7] *N. J. Geol. Survey*, 287 (1878).
[8] *Mo. Geol. Survey*, **11**, 104 (1896).
[9] *Ibid.*, **11**, 106 (1896).

Whilst a lamellar nature may be one factor in producing plasticity it is certainly not the only one to be considered, and it is very doubtful if it is of great importance, as more recent investigations suggest that the particles of clay consist of aggregates of intersecting needle-shaped particles of a crystalline nature, these aggregates producing masses having a very porous and open structure (see p. 265).

Effect of Aggregation of the Particles.—Evidence is accumulating which seems to show that the structure of the ultimate particles and their aggregation into larger ones has an important influence on plasticity, and it has even been suggested that plastic clays are composed of "crumbs," each consisting of a felted mass of lath-shaped or needle-shaped crystals. On the other hand, Aleksiejeff and Cremiatschensky have found that very fine-grained and very coarse-grained clays are both less plastic than those containing both large and small grains, and Mellor [1] suggests that a distribution of grains of various sizes which permits the closest possible packing gives a maximum plasticity, but Schurecht [2] appears to have found that—

(*a*) Loosely cemented aggregates of clay grains are more plastic than closely compacted ones.

(*b*) Fine-grained aggregates are more plastic than coarse-grained ones.

(*c*) Flocculated aggregates are more plastic than deflocculated ones.

(*d*) Flocculated aggregates are more plastic than cemented ones.

He states that the reason some clays retain their plasticity after removing the fine portion whilst others lose it, is due to the former consisting of loosely aggregated bundles of clay grains which can fairly easily be broken down by stirring, yielding a fresh supply of fine grains, whilst the cemented particles require a much greater force for their disruption. According to him, more of the finest particles can be produced in ball clays than in kaolins, because the flocculated aggregates in the former are composed of finer grains than in the latter, and for this reason a greater plasticity can be developed. Schurecht also found that the addition of an alkali to a clay-suspension increased the strength of ball clays in the dry state to a greater extent than that of kaolins; he attributed this difference to the finer particles composing the aggregate "crumbs" in ball clays.

Purdy agrees that the larger particles of clay are simply agglomerations of the smaller particles and possess the same properties.

Effect of Surface Area and Intermolecular Attraction.—On account of their fineness, grains of plastic clay have a large surface area and, consequently, exhibit surface phenomena (including intermolecular attraction and colloidal properties) to a very marked degree. It has long been held that the plasticity of some clays may be due to the mutual attraction of water and clay, so that each particle of clay becomes surrounded with a relatively thick envelope of water, whereas non-plastic materials appear able only to retain a much thinner film, which does not permit that movement of the particles over each other which appears to be an essential feature of plasticity. In other words, particles of clay and water appear to have so great a mutual attraction for each other that they naturally produce a sufficient amount of "lubricant"

[1] *Trans. Eng. Cer. Soc.*, **21**, 91 (1921–22).

[2] *Bull. Amer. Cer. Soc.*, 153 (1922).

(p. 258) around each grain of clay. A similar view is held by Zschokke, who considered that the surfaces of the grains are altered by the contact with water, forming a gelatinous material, which also facilitates the motion of the particles over one another (see *below*). Various investigators have shown mathematically that solid particles of the size of grains of clay may quite easily hold, by molecular attraction, the proportion of water present in plastic clays ; but, unfortunately, such arguments, when applied to feebly plastic clays, suggest that they should be as plastic as other clays. Hence, it appears necessary to introduce another factor, such as the colloidal state of part of the clay particles, in order that the plasticity of some clays can be rightly understood. Thus, Grout [1]—who attributes plasticity to molecular attraction and the action of colloids—has shown that it depends on—

(*a*) The distance clay particles can move upon each other without losing coherence, *i.e.* upon (i) the shape and size of the grains, and (ii) the thickness of the watery film through which they will attract each other.

(*b*) The amount of coherence or resistance to movement, *i.e.* on (iii) the friction of the films, and (iv) the friction of the grains upon each other.

Grout attempted to show that the amount of water required to develop the maximum plasticity is approximately that required to coat the grains of clay with a layer of water 0·00005 mm. thick ; Purdy considers it to be more than this and to be the amount required to produce the maximum thickness of film and to occupy the pores in the dry clay. It has been suggested that the particles of highly plastic clays are smaller than those of china clay and other lean clays and that, consequently, the former are able to retain more lubricant in proportion to the weight of clay, and thereby produce conditions favourable to plasticity. It is probable, however, that the matter is more complex than this.

Effect of Water and the Resulting Colloidal Phenomena.—It is probable that the best explanation of plasticity is one which attributes it largely to colloidal phenomena, for although many substances in the colloidal (gel) state are not plastic, all plastic substances possess many properties which are characteristic of colloidal materials.

It has already been shown (p. 258) that plasticity appears to be due to the presence of solid particles surrounded by a suitable proportion of viscous fluid which may or may not have the same composition. In the case of clays, the fluid appears to be colloidal, produced by the action of water on the smallest particles of clay, and possibly on any organic colloid matter which may also be present. Such a colloidal fluid would be more viscous than water and would possess all the characteristics necessary to enable it to unite with the minute, inert, solid particles of clay and so produce a plastic material, *i.e.* a material having properties intermediate between those of a solid and a liquid. P. Rohland [2] appears to have been the first to attribute the plasticity of clays to colloidal phenomena ; he regards plastic clay as consisting of very minute, amorphous, non-plastic grains or cores surrounded by films of material in the colloidal (gel) state, these films—when the maximum plasticity is developed—

[1] *W. Va. Geol. Survey*, **3**, (1905) ; *Trans. Amer. Cer. Soc.*, **14**, 71 (1912).

[2] *Zeit. für Anorg. Chem.*, **31**, Part I., 158 (1902).

being saturated with water. When the clay is dry, the colloidal matter shrinks and becomes hard and horny and its gelatinous properties are lost ; consequently, the solid particles cannot move over one another with the same facility as in the plastic paste. If, on the other hand, an excess of water is added, the gel is converted into the sol state and when sufficient water has been added, the clay is in suspension in the surrounding material and produces a clay slip. Rohland has further suggested [1] that the plasticity of a clay depends on the amount of hydrolysis which the material has undergone, so that kaolin, which is scarcely hydrolysed, has very little plasticity, whilst very plastic ball clays appear to have been highly hydrolysed. The amount of hydrolysis which can occur appears to depend upon the presence of free alkali in the water, a sufficiently high temperature and a very prolonged period of action. The necessity of all these three factors would explain why very pure clays, such as china clay and kaolins, cannot be made plastic by heating with water. In such clays, the free alkali is absent and the time available (even in experimental work) appears to be far too short.

This explanation of the cause of plasticity is confirmed by an experiment by Mellor, who found that if ground pottery, felspar, or Cornish stone is heated with water under pressure at a temperature of 300° C. for several days, a gelatinous coating is produced on the grains which renders them feebly plastic. This action, however, does not take place in the absence of alkalies, so that china clay and flint are not appreciably affected by the treatment. Koerner has shown that alumina becomes gelatinous when the finely-divided material is subjected to the action of water for a long period.

Separation of Colloidal Matter from Clays.—One of the difficulties of attributing plasticity to the presence of colloidal matter in clays is the small quantity of such matter which can be separated. T. Schlœsing,[2] in 1872, was the first to definitely report the presence of colloidal matter in clays, but he was only able to separate 0·59 grams of suspended matter from 40 grams of kaolin which has been allowed to settle for twenty-seven days. He found this superfine material possessed considerable cohesion, whilst the slightly coarser sediment had practically none, and so considered the finest material separated to be colloidal.

Several other attempts have been made to separate the colloidal matter from plastic clay by kataphoresis and other means. Thus, the finest suspended particles in a ball clay have been found by Mellor [3] to consist of a horny, glue-like material which is present to the extent of about 0·05 per cent. in Devonshire ball clays, but only about 0·005 per cent. was found in china clay. These proportions are extremely small and, what is equally remarkable, the clays from which these fine portions were separated appeared to be equally plastic before and after this removal. It is, of course, possible that the adhesion of the colloidal to the inert material is so great that the colloidal matter cannot be separated from the inner " core." The powerful cohesion may be due, as suggested by G. A. Bole,[4] to the films of colloidal matter

[1] *Sprechsaal*, **41**, 447 (1908).
[2] *Comptes Rendus*, **79**, 376–80, 473–7 (1874).
[3] *Trans. Eng. Cer. Soc.*, **21**, 91 (1921–22).
[4] *J. Amer. Cer. Soc.*, **5**, 469 (1922).

having an opposite polarity to that of the solid grains or cores which they surround. If this were correct, the addition of an electrolyte of similar polarity to the clay-grains would attract and separate a portion of the colloidal matter and so would decrease the thickness of the films covering the clay grains, and would enable the latter (on account of their like polarity) to repel one another and so increase the dispersion of the clay, whilst the addition of a flocculating agent would have a contrary effect and would increase the thickness of the films and cause the particles to be compacted together.

In some clays, a very small proportion of colloidal silica may be abstracted, either by water or by boiling the clay with dilute sodium carbonate. The proportions found by the author have usually been extremely small, except in the case of some very impure brick earths, some of which contain as much as 4 per cent. of colloidal silica. The addition of colloidal silica to a china clay does not appreciably increase the plasticity of the latter, but this may be due to the fact that, unlike most organic colloids, it has very little elasticity.

The presence of some other colloidal substances increases the plasticity of a clay, though when such substances are added artificially the product is not the same as a natural, plastic clay. Among others may be mentioned *bentonite*, which very closely resembles a colloidal solution when suspended in water, but it has a low binding strength, does not appreciably increase the plasticity of clay mixtures, and also lacks adhesiveness and cohesion. Such a material cannot, alone, be regarded as a cause of plasticity in clays. Similarly, various organic colloids which may be added, including tannin, humus, and various glues, starch paste, etc., and H. Spurrier has found that the addition of hydrogen peroxide increases the amount of carbon dioxide evolved from a clay paste and facilitates the growth of algæ, the resultant paste having a greater plasticity than formerly. The presence of organic matter is not, however, the only cause of plasticity, as china clay contains scarcely any organic matter and yet is appreciably plastic.

Van Bemmelen has shown that if active organic colloids were originally present in a clay they would soon lose their properties, whereas the plasticity of a clay persists, and from this he contended that plasticity was not in any way connected with colloidal phenomena. Few present-day investigators would go so far as this; the present tendency is rather to agree with Sven Oden,[1] who considers that there is no special chemical colloid which predominates in clay, but that the colloidal matter consists of the mineral constituents of the clay which have been changed from the crystalline into the amorphous or colloidal condition.

Herman, Rosenow, Purdy, and others consider the effect of colloids in producing plasticity is much less than is usually supposed, and attribute it to such wholly physical properties as the porosity of the clay particles, or to adsorption, solution, molecular attraction, and high surface tension. Purdy states that the volume of water required for the development of the maximum plasticity is precisely the amount required to fill the pores of the dried mass and also to enclose each particle or bundle of particles in a film of water of the maximum thickness for it to retain by molecular

[1] *Trans. Faraday Soc.*, **17**, 328 (1922).

attraction. Most of those who object to the view that colloids play an important part in causing plasticity rely on a single property which is characteristic of some colloidal materials, though such critics appear oblivious of this fact. Thus, it is rather foolish to object to the theory that plasticity is largely due to the presence of a colloidal film, and yet to suggest that it is due to the plastic clay grains having an abnormally large surface area, great adsorptive power, or other properties which are essentially colloidal in character. It is much better to adopt the attitude of Rosenow,[1] who is opposed to the colloidal theories hitherto published, but admits that a suitable colloidal theory would explain the facts if only it could be found; or that of Mellor, who considers that the known facts favour the colloidal theory as the best qualitative explanation, though no one has yet succeeded in demonstrating this theory quantitatively.

The view as to the cause of plasticity most favoured by the author is that it is due to the simultaneous presence of two substances or groups of substances in suitable proportions, the substances being as follows :—

(*a*) Non-plastic particles composed of minute crystals so placed as to form felted balls of a highly porous nature. Such " balls " would be crystalline, as clays have been found to be so by Johnson and Blake, Ashley, Bragg, etc., but would differ from minerals such as quartz, mica, etc., in the physical structure. The " balls " of clay form a porous, felted mass, whilst the other minerals form a laminated structure which cannot be made highly porous, no matter how finely they are ground, and so they can only retain a small proportion of colloidal gel on their surface, whilst the porous " balls " are composed of lath-like crystals so tangled and interlocked as to have a roughly globular shape with a very large surface, which can retain a relatively large amount of adherent water not merely on the spherical surface, but also on the surface of the individual crystals and in the pores between them. As the amount of water so held increases, some of the clay crystals may separate, forming a few plate-like or laminated masses which would account for some of the properties of clay. It is also very probable that the crystals themselves have a space-lattice structure, those clays having the most open or porous molecules having a greater plasticity than those with simpler or more closely packed molecules.

(*b*) A colloidal (gel) material forming a film on the surface of the crystals and occupying the interstices between them. This colloidal material may be of complex composition or it may be the product of the action of water (hydrolysis) on the smallest particles or even on individual crystals of clay. Colloidal sols and gels are often of very low concentration—an ordinary table jelly which is quite firm only contains about 3 per cent. of true solid matter, and in the presence of a spongy material much lower concentration will suffice—and in addition to the viscosity and adhesion of a colloidal gel, the force of molecular attraction between the clay crystals and water appears to be so great as to enable them to fill and surround themselves with a relatively thick film of water and so form a series of globules which possess many of the properties of a colloidal gel.

It appears probable that a material so constituted of porous balls and a viscous

[1] *Tonind. Ztg.*, **35**, 1261 (1911).

fluid would possess all the characteristic properties of a plastic paste, including viscosity, deformability, the retention of shape when the deforming force was removed, etc. If such a material were to be dried it would also behave like a clay paste and would also be capable of reconversion into a plastic paste provided its constituents were not decomposed in the drying. If the colloidal gel were composed of silica, alumina, alumino-silicic acid, or other suitable mineral, the mass of " balls " and gel would harden on drying and burning in a manner similar to plastic clay.

The above conception of the clay particle appears to fulfil all the phenomena characteristic of clay pastes and it overcomes the very serious objection raised by various investigators to the small amount of colloidal matter obtainable from clays. If, as appears probable, the " balls " are of various sizes, a material of such a constitution would possess the properties to which so much importance is attached by Purdy and Schurecht, *i.e.* the clay " balls " would be composed of aggregates which could be dissociated gradually, the larger particles possessing the same properties as the finest grains which remain in suspension indefinitely when a clay is mixed with sufficient water. The chief objections to this structure are :—

(i) The existence of balls of felted crystals cannot be directly proved.

(ii) If a clay is completely suspended in water by the aid of an electrolyte, such as soda, it is somewhat surprising that the " balls " are not broken down into their constituent crystals. If it is assumed that the " balls " are sufficiently small to be invisible even under the most powerful microscope, both these objections disappear. If it is further assumed that the " balls " may aggregate into still larger particles, the behaviour of plastic clays when the finest particles have been removed would be explained. The treatment of the material from which the finest " balls " had been removed would result in the disintegration of some of the aggregations of " balls," with the result that other, smaller " balls " would be produced. This could go on almost indefinitely, *i.e.* until the clay consisted entirely of loosely aggregated " balls," which would be highly suspensible. In practice, no clay can be completely reduced to this state, because various impurities such as quartz, mica, etc., are present in addition to the true clay, and the past history of the clay itself has much to do with the properties of the grains. Thus, a metamorphosed or indurated clay would obviously be less likely to be deflocculated than a highly plastic ball clay.

Most commercial clays consist of three kinds of material :—

(*a*) Deflocculated grains which can remain in suspension for an indefinite period.

(*b*) Flocculated or cemented aggregates of similar grains which can be partially deflocculated.

(*c*) Coarse, non-plastic impurities such as quartz, mica, felspar, etc., which are too large to remain in suspension in water.

Even the purest clays are not wholly colloidal, but probably consist—as has been suggested above—of non-colloidal " balls " and a colloidal film. If this is correct, the difference between a pure colloidal gel and a plastic clay is obvious, as the former contains no inert (non-colloidal) grains like the latter.

Increase and Reduction of Plasticity.—Many natural clays are potentially rather than actually plastic ; their plasticity may, therefore, be increased, up to a

limit, by mixing them with a suitable proportion of water. Some clays, on the contrary, are too plastic to be used in their natural state, and must, therefore, be treated in some way so as to reduce their plasticity.

These changes in the actual (as distinct from the potential) plasticity of a clay are of great importance in its utilisation. To increase the potential plasticity of a clay, however, is extremely difficult and it apparently requires a far longer time (p. 236) than is practicable when artificial means are employed. A clay or clayey mixture is usually regarded as having attained its maximum plasticity when a portion of it, after being squeezed in the hand, retains an impression of all the fine lines on the skin, yet leaves no appreciable quantity of clay adhering to the fingers. If a clay in this state is mixed with a little more water, it becomes sticky and adhesive, and if still more water is added progressively the clay eventually becomes obviously fluid and devoid of plasticity. A dry piece of clay is equally devoid of plasticity, as it is too rigid to be deformed by squeezing in the hand and if subjected to a greater pressure it cracks and may fall to pieces. Between these extremes of rigidity (of dry clay) and fluidity (of a clay slip) are innumerable gradations of plasticity and stickiness, depending on the nature of the clay and on the proportion of water added to it.

It also follows that each clay or mixture has an individual maximum potential plasticity depending on the nature of the clay. Thus, a china clay cannot, by the artificial addition of more water, or other substances, possess the same maximum potential plasticity as a first-class ball clay. The actual plasticity of a sample of each clay may be the same if, for example, that of the china clay has been fully developed, whilst the ball clay is in a semi-dry state and of low actual plasticity because it does not contain a sufficient proportion of water.

Many attempts have been made to ascertain what proportion of water should be present to develop the full plasticity without making the material " sticky." Stickiness is described by Ashley as the quality developed by plastic bodies when the granular constituents are removed. It may also be described as a property characteristic of a material which is in a state intermediate between a plastic solid and a viscous liquid (see p. 267). " Sticky " clays adhere to any solid material with which they may come into contact, whilst a plastic clay will part cleanly from such substances.

A sticky clay, when partially dried or when mixed with non-plastic material, becomes less sticky. Some clays are naturally sticky rather than plastic, as, for example, those found in the geological formation known as " London clay." They can only be used industrially when too little water is present to develop their plasticity fully, or by adding a non-plastic material so as to lower their plasticity. In other words, the point at which a clay begins to lose its plasticity and becomes sticky is that at which rather more water has been added than the maximum which can be retained by the intermolecular attraction of the solid particles. In practice, the maximum amount of water is found by adding water progressively in small quantities to a known amount of clay, mixing the clay and water together, and squeezing the mass in the hand as described above. Eventually a mass will be obtained which conforms to the description given, and if a further small quantity of water is then

incorporated with it, the mass adheres to the hand, showing that an excess of water has been added. Practical men who are constantly handling clay pastes can tell within a small amount what is the correct quantity of water to use with a given clay or mixture in order that it may have a suitable amount of plasticity.

Atterberg made an elaborate subdivision of what may be termed the *range of plasticity* into five stages as follows :—

(*a*) The upper limit of fluidity, at which the clay flows almost like water.

(*b*) The lower limit of fluidity, at which two portions of the material will not flow together and unite by themselves when jerked and shaken.

(*c*) The adhesion limit, at which clay ceases to stick to other objects, such as the hands when the clay is squeezed.

(*d*) The " rolling-out limit," at which the clay ceases to be capable of being rolled out into thin cylinders or threads.

(*e*) The " cohesion limit," at which the grains cease to cohere to one another.

The range of suitable consistency for working lies between (*c*) and (*d*).

Atterberg found that the flow-limit and rolling-out limit coincide in non-plastic loams, but as the plasticity of a clay increases these two limits become more and more separated and so constitute the working range of plasticity. He also found that the adhesion-limit is raised by an increase in the proportion of organic matter, but the total plasticity is reduced. Thus, in clays and loams containing much humus, the adhesion-limit is considerably higher than the flow-limit. Where humus is present in only small quantities, or is absent, the adhesion-limit is lower and in the most plastic clays it lies below the flow-limit and, consequently, in such materials the range of plasticity is between the rolling-out limit and the adhesion-limit as previously stated. The addition of sand to clay lowers the total plasticity by reducing the range of plasticity, though the adhesion-limit is raised relatively to the others.

From a consideration of the foregoing, Atterberg has suggested that the plasticity of a clay mixture may be expressed numerically by deducting the percentage of water corresponding to the rolling-out limit from the percentage of water corresponding to the flow-limit. Thus, if 60 per cent. of water is required to cause the material to flow and 30 per cent. is necessary to enable it to be rolled out into cylinders, its plasticity number (*Atterberg Number*) 60—30=30. He proposed to group clays into four classes :—

	Atterberg Number.
Class I	17–27
Class II	5–15
Class III	4–7
Class IV	0–1

This method attributes to some substances, such as barium sulphate, a high plasticity, though they are not generally considered to be highly plastic. Atterberg's numbers also correspond very closely to the binding power of clays (p. 281), rather than to their true plasticity, and R. Rieke [1] has pointed out that Atterberg's ranges

[1] *Sprechsaal*, **44**, 597 (1911).

are not always reliable, the plasticity being due to other properties than those considered by Atterberg.

Rieke, with Seger and others, considers the firmness of the dried material to be a necessary property of truly plastic materials, but this is not correct, as the properties of the dry clay are no guide to the plasticity of the clay paste. The mistake has arisen through confounding " binding power " with plasticity ; a clay to be of value industrially must usually possess both these properties and, in addition to being plastic and easily moulded when in the form of a paste, it must form a strong and compact mass when dried and burned. Such a complex of properties is not required in other plastic materials.

The **proportion of water required** to produce the maximum plasticity in any clay varies according to the extent to which the clay can be made plastic. Thus, a dry clay, which is potentially highly plastic, such as a ball clay, requires much more water to develop its plasticity to the fullest extent than a clay whose total potential plasticity is low. Table C gives figures which are applicable to various clays, but no closely concordant figures can be obtained, as clays vary so greatly :—

TABLE C.—*Water Required to Develop Plasticity*

Material.	Percentage of Water Required.	Material.	Percentage of Water Required.
Brick clays . .	15–25	Flint clays . . .	15–24
Fireclays . . .	15–35	China clay and Kaolins	18–50
Shales . . .	15–25	Ball clays . . .	25–50
Pottery clays . .	15–50	Zirconia with starch bond	8–12

The amount of water required to make a suitable paste is dependent to a large extent on the nature of the particles constituting the mass. Thus, coarse particles will require less water than fine-grained clays and the maximum plasticity is developed in an " aged " paste with less water than is required for a freshly made one, because in the " aged " paste the water is more uniformly distributed.

The presence of soluble salts and organic matter also influences the amount of water required to develop the maximum plasticity. Thus, the addition of alkali usually decreases the amount of water required to develop plasticity, but under some conditions Rohland [1] found that the addition of alkali to some clays increased the amount of water required.

Calcium hydroxide also increases the amount of water required. Magnesia, lime, strontia, baryta, and some of their carbonates and sulphates, when these are sufficiently soluble to be present in an appreciable proportion, generally increase the amount of water required to develop the maximum plasticity. H. G. Schurecht also found that acids in small quantity increase the water required to develop plasticity, but larger

[1] *Die Tone*, p. 85.

amounts decrease it. Bleininger and Fulton,[1] however, found that acids decreased the water of plasticity, *i.e.* decreased the drying shrinkage. This is contrary to the results obtained by Rohland. The presence of various organic materials, such as tannin, also reduces the amount of water required.

The proportion of water required to develop the maximum plasticity also depends on the pressure used in testing the plastic paste. Thus, a paste for hand-moulded bricks must be softer and usually more plastic than that used for machine-pressed bricks. J. W. Mellor [2] found that with different pressures the maximum plasticity of a certain clay occurred with the following proportions of water :—

TABLE CI.—*Effect of Pressure on Plasticity*

Pressure, kg. per sq. cm.	Water, per cent.	Pressure, kg. per sq. cm.	Water, per cent.
200	5·6	50	19·2
150	8·8	25	23·0
100	12·5	1	26·4

Bourry [3] gives the following figures for the water required to produce a suitable paste for moulding in different ways :—

TABLE CII.—*Water required for Different Moulding Processes*

	Percentage of Water Required.		Percentage of Water Required.
Dry body . .	7–18	Half soft body .	15–30
Stiff body . .	10–20	Soft body . .	17–35
Half stiff body .	12–25	Liquid body .	20–40 or more.

He found that with material of a definite consistency, when subjected to a definite pressure, the plasticity must be within certain limits to produce sound articles ; if the mass is too plastic it will stick to the mould and if it is too " short " it will not be sufficiently well compacted to produce strong articles.

The effect of non-plastic materials is usually to reduce the potential plasticity

[1] *Trans. Amer. Cer. Soc.*, **14**, 827 (1912).
[2] *Trans. Eng. Cer. Soc.*, **21**, 25 (1921–22).
[3] *Treatise on the Ceramic Industries*, trans. by A. B. Searle (Scott, Greenwood & Son).

of any material to which they are added. Consequently, the proportion of water required to make a plastic paste of good working consistency is also reduced, as are the tensile and crushing strengths, but the porosity after firing is usually increased.

The **effect of organic matter** on the colloidal properties of clays has already been described (pp. 244 and 249). It will be seen that it may have one of two effects : (*a*) to introduce acids into the clay, which flocculate the colloids present ; or (*b*) to increase the amount of colloidal matter present. In both cases it increases the plasticity if the organic matter present is not in too large a quantity. Clays containing much organic matter are often highly plastic. Hard, compacted clays containing much organic matter may also develop a high plasticity on mixing them with a suitable proportion of water, allowing them to " age " and then tempering the paste.

The **effect of adding colloidal matter** to a slightly plastic clay or ceramic material cannot always be predicted with certainty. The addition of *organic colloids* has been dealt with above. A. S. Cushman [1] found that colloidal alumina increased the plasticity of clays, but F. F. Grout found that when such masses are dried they are very feebly bonded.

Colloidal iron hydrate has been found to increase the plasticity of clays, but colloidal silica appears to have little or no such effect.

Increasing Plasticity.—The investigation of methods of increasing the plasticity of clays and ceramic materials is beset with many difficulties ; among others is the difficulty of distinguishing between the actual plasticity of a mass and the potential plasticity which may be developed by various means, such as incorporating a suitable proportion of water or storing the material under conditions which will ensure the uniform distribution of the water present and by the possibility of actually increasing the plasticity by converting some of the non-plastic materials present into plastic ones, or by the addition of some substance which definitely increases the total amount of plastic material present.

The plasticity of a ceramic material may be increased—

(*a*) By the addition or removal of a suitable proportion of water.

(*b*) By the more thorough incorporation of the water and plastic materials present.

(*c*) By the removal of some of the non-plastic material present (usually by converting the material into a slip, allowing some of the non-plastic matter to " settle out " and then removing the excess of water from the decanted slip).

(*d*) By the addition of any substance which, on fermentation or other decomposition, produces a free acid, *e.g.* peat, cellulose extract, etc.

(*e*) By the addition of any substance of a colloidal gel nature, or one which is converted into such a substance on prolonged storage, *e.g.* colloidal silica, alumina, or iron hydrate, hot starch, dextrin, tannin, rubber, sumach, inulin, caramel, gelatin, gum, glycogen or various ferments and enzymes ; the plasticity of clay may be increased, but care must be taken to avoid confusion between true plasticity and

[1] *Trans. Amer. Cer. Soc.*, 6, 7 (1904).

the pseudo-plasticity caused by the addition of materials of an oily, gelatinous or gummy nature.

(*f*) By the addition of a weak acid such as gallo-tannic, acetic, or humic acid, or of crude extracts containing one of these or other weak acids, such as peat extract, straw extract, etc.

(*g*) By the addition of any flocculating or coagulating agent (p. 243).

(*h*) By an electrical treatment which will reverse the electric charge in the material.

(*i*) By grinding and pugging with water, which increases the hydrolysis and, therefore, the number of flocculating ions in the mass.

(*j*) By the process known as " ageing " or " souring " (p. 274).

Reducing Plasticity.—The plasticity of a ceramic material may be reduced by the converse of any of the methods just described, viz. :—

(i) By the removal of a sufficient proportion of water, or by adding sufficient water to convert the plastic material to a slip. This method affects the actual, but not the potential, plasticity.

(ii) By insufficiently mixing the various ingredients of a ceramic mixture.

(iii) By the addition of non-plastic material, such as sand or grog, the effect of which is to distribute the plastic material through a larger volume, *i.e.* direct reduction of plasticity by dilution.

(iv) By any process which suitably increases the proportion of free hydroxyl ions, *e.g.* the addition of a deflocculating agent such as sodium carbonate (p. 247).

(v) By any electrical treatment which has the same effect as a deflocculating agent.

(vi) By heating the material to 200° C. or to any other suitable temperature. This is usually the simplest and most effective means of reducing plasticity, and it has the further advantage that the plasticity so lost cannot be regained.

Rohland has suggested that any treatment or addition which results in an increase in the number of hydroxyl (OH) ions will reduce the plasticity of a ceramic mass, and that any means which increase the number of hydrogen ions will also increase the plasticity. This statement, whilst of wide application, does not appear to be of quite such general use as Rohland has suggested.

Plasticity and Viscosity.—Plasticity appears to be closely related to viscosity, and it has been suggested that plasticity may be estimated from the measurements of the viscosity of a material. Thus, Bingham and Green have suggested that the only difference between the flow of a viscous liquid and of a plastic substance under pressure is that, with the former, the flow starts on the application of any pressure (no matter how small), whilst with a plastic substance the flow does not start until the applied pressure has reached a definite amount depending on the plasticity of the material. A. de Waele has shown that this is incorrect and that the analogy between plastic bodies and viscous liquids is very simply shown by the following relationships :—

Liquids under normal shear have $\frac{P}{Q}$ constant, whilst plastic bodies have $\frac{P}{Q^n}$ constant, where P is the applied pressure, Q is the volume discharged from the

viscometer, and n the exponent representing the degree of plasticity; n is always less than unity.

From this it follows that a plastic substance will become a viscous fluid (even though it may retain its "solid" appearance) when $n=0$. In the case of clay or mixtures which owe their plasticity to clay, this change occurs when sufficient water is added to the material. A. De Waele's [1] work also shows why there is no sharply defined demarcation between a soft plastic clay and a slip made from it by the addition of water.

A. S. E. Ackermann [2] found that when sufficient pressure is applied to clay it will flow like a liquid, *i.e.* when a disc is pressed into a clay mass a critical pressure is reached, after which, without any increase in the pressure, the disc continues to sink at ten times the previous rate. This critical point, which he terms the pressure of fluidity, may be calculated from the formula

$$P = \frac{L}{\frac{\pi}{4}D^2},$$

where L is the critical load and D is the diameter of the disc, which may conveniently be rearranged in the form

$$P = 1{\cdot}275a,$$

where $a = \frac{L}{D^2}$.

The mean radial speed of flow of the clay from beneath the edge of a disc is about one-eighth the speed of penetration of the disc. The mean speed of penetration of a disc into clay when the load is just sufficient to produce the pressure of fluidity is about 1 cm. per minute. When a disc penetrates clay there appears to be a stagnant "cap" of clay immediately under the disc which travels down with the disc. Even under considerable tangential stress there is no progressive strain in the case of clay containing 25 per cent. of water. In other words, according to Ackermann, it then behaves as a solid and not a fluid.

The proportion of water in a material has a great influence on its rate of flow. The reason a dry sand or ground clay, which flows readily, forms a highly viscous material when mixed with a little water is that when one material is dispersed in another, the viscosity of the mixture is greater than that of the disperse medium. This phenomenon is observable under widely different circumstances, so that even a gas, when dispersed through a suitable liquid, will yield an apparently solid product, as when liquid white of egg is "whipped" to a "foam." Another example is the greater viscosity of a molten silicate containing a larger quantity of air enmeshed in it than the viscosity of the same silicate when free from air.

When clays have larger proportions of water the rate of flow increases with the amount of water present. Table CIII shows the results Ackermann obtained for London clay with varying percentages of water.

[1] *Faraday Soc.*, Meeting 1923. [2] *Loc. cit.*, p. 126.

TABLE CIII.—*Pressure of Fluidity of London Clay*

Per cent. Water.	Pressure of Fluidity in kilos. per sq. cm.	*a*.
37·8	0·107	0·083
37·0	0·128	0·100
31·0	0·320	0·251
30·0	0·527	0·414
29·0	0·600	0·471
28·0	0·846	0·663
25·4	1·938	1·521
23·6	4·700	3·690
22·0	7·200	5·650

He found that the " pressure of fluidity " was decreased about 25 per cent. as a result of boiling the clay ; that is to say, clay, when boiled, becomes more workable. In this connection, he has pointed out that much the same result could be obtained by the mere lapse of time. Clay when stored for a considerable period has very much the same properties as when boiled.

Ackermann also found that when clay is discharged under pressure, through sharp-edged circular orifices, the rate of discharge increases more rapidly than the rate of increase of pressure, and ultimately there is a phenomenon analogous to the pressure of fluidity, which has been called " the critical pressure of extrusion."

In mass flow (as distinct from surface flow) high pressures are necessary to overcome at the same instant the resistance due to cohesion of myriads of molecules throughout the mass. It is not always recognised that in mass flow the function of the high pressure is to produce molecular movements throughout the mass. The effect of pressure is to reduce the volume by elastic compression and thus to store energy which will become kinetic if the mass is allowed to expand through a small opening. Thus, if a mass of clay is compressed in a cylinder which it just fills, it will store up a large amount of energy by elastic compression. If a small hole is bored in the cylinder the clay will flow out like a liquid. The fluidity lasts long enough to enable the clay to pass through the hole, after which it behaves as a solid.

Beilby's experiments (on gold) have shown that a single blow, if sufficiently rapid and sufficiently powerful, will probably reduce a substance immediately to a homogeneous liquid. A similar effect may possibly occur when pressure is applied to clay.

Souring or " **ageing** " is a change which takes place in clay pastes and is dependent to some extent on their colloidal nature. When a clay paste is kept moist and cool for a sufficiently long time its actual plasticity is increased, the water in it is more uniformly distributed, and the homogeneity and working properties of the

clay are greatly improved. Hence, where financial considerations permit, clay pastes are greatly improved if they are allowed to "sour." In order that the souring may be effective an ample quantity of water must be present, and to ensure this, and to prevent surface drying, the clay is usually covered with wet cloths during the souring period, the cloths being renewed or rewetted at frequent intervals. Sometimes the clay is placed in pits or in sumps and covered with water for the required period. The surplus water is afterwards run off and the paste is dug out. Wedgwood and some other famous pottery manufacturers have aged the moist clay by keeping it stored in air-tight boxes for several years.

The effect of ageing or souring is probably chiefly due to the decomposition of the organic matter present, with the formation of dilute acids which coagulate the fine grains of clay and thus increase the plasticity. A similar effect may sometimes be obtained by adding acid direct to a fresh clay; but the results are not quite the same, as when decomposition occurs *in situ* the acid is more uniformly distributed, whereas when added artificially it must be allowed a considerable time before it is thoroughly distributed through the mass.

The presence of an excess of free alkali in clays limits or may even prevent their improvement by souring. Any such excess should be neutralised by the addition of a suitable acid before any increase in the plasticity of the clay can occur. Seger suggested the addition of a suitable proportion of acetic acid to clays before souring, whilst the addition of old vinegar and of wine was, at one time, a common practice amongst some pottery manufacturers.

It has been suggested that the effect of bacteria or moulds present in a clay has an important effect in the souring, but the extent of their influence is not definitely known. In order to increase the proportion of fermented matter some manufacturers have added sugar or honey to their pottery mixtures before souring.

The effect of heat on the souring process is difficult to determine on account of the complexity of the reactions which occur. Rohland has stipulated that the souring should take place in a cool atmosphere, as it is fundamentally a colloidal phenomenon, yet clay slips which are dried by heat are more plastic when re-wetted than those which have had the surplus water removed in a filter press; and H. Spurrier [1] has found that when souring or ageing clay a temperature of 80–90° F. is preferable to one below 60° F., as the plasticity is increased to a greater extent; A. S. Watts [2] has also found that the best conditions for ageing clay are a temperature of 80° F. and a relative humidity of 90 per cent.

Pseudo-plasticity.—A modified form of plasticity may be developed in some non-plastic materials by the addition of a suitable viscous fluid, such as oil or, preferably, an aqueous solution of a gelatinous or gummy material, such as hot starch, dextrin, rubber, sumach, inulin, caramel, gelatin, gum, glycogen, various ferments and enzymes and other colloidal materials.

Such an addition increases the plasticity of the material, but does not produce the same result as plastic clay in the fired material, because such organic additions

[1] *J. Amer. Cer. Soc.*, **4**, 113–118 (1921).
[2] *New Jersey Ceramist*, **1**, 93 (1921).

are burned out in the firing. For this reason, such substances are said to produce a *pseudo-plasticity* which must be carefully discriminated from that of natural plastic clay. It is important when using such materials to increase the plasticity of a substance, to use a suitable proportion of each. An excess will usually produce " stickiness " (p. 267) rather than plasticity.

Oiliness is sometimes regarded as a form of pseudo-plasticity, though it is really distinct both from true plasticity and from stickiness. It is often due to the presence of oils or oleaginous substances, and, where necessary, may usually be removed by extracting these materials with benzene or other suitable solvent. The oleaginous nature of some clays is destroyed when they are boiled with a solution of alkali which forms a soap ; the latter increases the pseudo-plasticity (p. 275) of the clay. The " oiliness " of some clays is more readily observed when an attempt is made to mix them with water.

Mobility.—The mobility of a clay or clayey paste depends on its plasticity and on the extent to which the solid particles are separated by water. If the plasticity is low, or if sufficient water is not present, the material will be largely immobile, but a highly plastic paste, or one containing a large proportion of water, is readily mobile. In the case of a plastic paste, pressure is required to make the material move, but a slip is as mobile as any fluid of the same character.

As the mobility is not strictly proportional to the percentage of water present, it is not desirable to include in any mobility-coefficient an expression for the water present in the mass. In other words, the mobility should be determined on an actual sample and either its consistency or the percentage of water in it should be stated quite independently of any figure for the mobility.

The mobility of a clay slip is the converse of its viscosity (see p. 290).

Extensibility.—Closely allied to the mobility and viscosity of a clay paste is the facility with which it can be made into certain useful shapes by extrusion through a die or mouthpiece, as in the manufacture of pipes, etc. In order that the extruded products may be commercially useful, the material to be extruded must be plastic as well as mobile, so that no simple factor can be used to express its extensibility. Probably the simplest mode of expression is in terms of viscosity, *i.e.* in the ratio between the quantity extruded in unit time and the pressure required to extrude ; but the size and shape of the aperture have so important an influence that it is almost impossible to reduce these to simple terms. In practice, the relative extensibility of various clay pastes must be expressed in terms of viscosity, the shape and size of the aperture being strictly defined. Thus, a paste which is quite satisfactory for the production of bricks by extrusion may be almost useless for the production of pipes or blocks of special shape by the same process.

Measurement of Plasticity

The plasticity of a paste cannot be determined and expressed by a single figure, as it appears to depend on so many different factors. For this reason, no exact scientific test has yet been devised for expressing the plasticity of a clay. Whichever

of the available methods are used, care must be taken to distinguish (*a*) the potential plasticity, *i.e.* the plasticity which the material possesses after such treatment as will develop the maximum plasticity apart from the addition of any substance other than water, and (*b*) the actual plasticity of the material when no water or other material is added. Thus, a dried clay may have no actual plasticity, but a very high potential one. Before describing various methods of measuring plasticity it seems desirable to explain that several methods which have been used for this purpose do not measure the plasticity. Thus, it is impossible to use any of the properties of dried clay to indicate the plasticity of clay pastes, though it is an interesting coincidence that the tensile strength of a dry clay is often proportional to the plasticity of the paste. The plasticity can only be measured by means of some property possessed by the plastic paste.

It is equally unsatisfactory to measure the " binding power " of a clay or clay mixture and to regard that as an indication of the plasticity, because there is no necessary connection between binding power and plasticity. It is even doubtful whether the proportion of colloidal matter present (p. 263) is a true measure of plasticity.

If plasticity may rightly be defined in terms of deformability (p. 144), it is clear that the only rational methods of measuring plasticity must be of a mechanical nature, and that they must measure the pressure required to alter the shape of the plastic mass to a definite extent within a definite period of time. Other methods which do not involve these three factors of force applied, change of shape and duration of force, may be convenient for various purposes, but they are not true measures of plasticity.

Indirect Methods.—For the reasons just stated, the following methods are not direct measures of the plasticity :—

(*a*) *The proportion of water required to develop a paste of recognisable consistency*, as suggested by Atterberg (p. 265) and others.—In addition to being indirect, Atterberg's method leaves a large margin for the personal element and is, therefore, undesirable, though it is convenient and has been largely used for comparative tests. It is based on the idea that the plasticity of a material is proportional to the amount of water present, but as it is not the water alone, but the nature of the viscous fluid (of which the water is only one constituent) and the nature of the solid particles as well, which determines the plasticity of a mass, Atterberg's method is fundamentally unsound.

The same is true of similar methods suggested by Simonis, Bleininger, and some other investigators, which are based on the idea that the amount of water required to make a slip of definite viscosity is a measure of the plasticity of a clay. This is not correct, because the amount of water required to produce a slip of definite viscosity may be only a measure of the amount of coagulable colloidal matter present, and because there is no simple relation between this and the viscosity and the plasticity.

(*b*) *The proportion of colloidal material present.*—Rohland considers plasticity to be proportional to *coagulable colloids*, the coagulable colloids being estimated from the amount of water required to develop a suitable consistency for moulding. This is an

attempt to measure the ratio of non-plastic core to colloidal (gel) film in each particle, and as these appear to be the two factors on which plasticity fundamentally depends, this method ought to be one of the best of the indirect methods. Unfortunately, it fails largely as a result of the difficulty of determining with certainty the proportion of coagulable colloids. A similar objection applies to Ashley's suggestion that the plasticity of clay may be measured by the ratio—

$$\frac{\text{Relative colloids} \times \text{percentage linear shrinkage of clay}}{\text{Jackson-Purdy surface factor.}}$$

Ashley endeavoured to determine the colloidal matter by measuring the amount of malachite green dye adsorbed by a definite quantity of the material, and calculated the " relative colloids " by regarding the amount of this dye adsorbed by a given weight of Tenessee ball clay as equal to 100, and the dye adsorbed by the sample as a percentage of this. The method used is described on p. 240. The shrinkage was measured in the usual manner. The method of calculating the surface factor is described on p. 56. The objections to Ashley's method as a measure of plasticity are as follows :—

(*a*) The plasticity is not due entirely to the presence of colloidal matter, yet this test merely measures the amount of colloid in the clay. It is also doubtful whether this method measures the whole of the colloidal matter present.

(*b*) Clays may contain more than one kind of colloidal matter which may adsorb dyes to different extents and, consequently, no true comparison can be made.

Although, as a result of his work on soils, N. M. Comber has stated that the plasticity of a clay is directly proportional to the volume of the deposit formed by making a suspension of the clay alkaline with ammonia and then adding calcium nitrate as a flocculent, and, therefore, directly due to the ratio of emulsoid coating to solid core in the clay particles, this cannot be regarded as a satisfactory method of determining plasticity.

Direct Methods.—The direct methods for measuring the plasticity of a material are necessarily of a mechanical nature ; they involve three variables : force, shape, and time.

One of the earliest of these methods, which, in spite of its crudity, is still largely used and is very convenient, consists in pressing a small piece of the material in the hand. A paste of a satisfactory consistency for moulding should not adhere to the fingers or palm, yet it should retain the marks produced on it by the lines on the hand. An excess of water will cause stickiness, whilst too little water will produce a mass which will not properly take an impress of the fine lines of the hand. This method of determining the plasticity of materials by their " feel " is satisfactorily employed by those who are continually handling clay, but it is unsatisfactory as a scientific test, as it introduces too much of the personal element, and the essential factors of pressure, changes of shape, and duration of pressure are not accurately defined. The same is true of the " rolling-out test," in which balls of clay of a prearranged size or weight are rolled into strips of convenient size and then wound into a coil. The less plastic clays soon crack and may thus be distinguished from the more plastic ones.

Strictly, this test depends more on the binding power than on the true plasticity of the clay.

Other tests which are less objectionable in this respect are :—

(*a*) *Extrusion Methods.*—Many years ago, Bischof [1] suggested that plasticity may be determined by measuring the length of a column of paste which may be extruded from a die before fracture of the extruded column occurs. This is closely allied to the measurement of the viscosity of a paste, but the method as devised by Bischof was too crude to be accurate. It may be greatly improved by measuring the pressure per unit area applied to the clay and by weighing the amount of material extruded in unit time. Then, according to A. de Waele (p. 272), the plasticity may be found from

$$\frac{P}{Q^n} = K,$$

where P is the pressure applied, Q the amount of paste extruded in unit time, K is a constant, and n the plasticity coefficient. This may be more conveniently expressed as

$$n = \frac{\log P - \log K}{\log Q}.$$

Any suitable form of viscometer may be used, provided it is strong enough to withstand the pressure. The latter may be applied by air from a compression chamber.

This method includes all the three essential factors (p. 277), the " change of shape " being that necessary to force a given quantity of material through a short capillary tube.

As explained on p. 272, the rate of flow or viscosity is not proportional to the plasticity.

(*b*) *Extension Methods.*—Several investigators have suggested that the extensibility of a paste or its tensile strength are proportional to its plasticity. Neither of these is alone sufficient, but a more accurate measure may be obtained by using Zschokke's suggestion and multiplying the percentage of extensibility (p. 142) by the tensile strength of the material. If the tensile strength is determined under constant conditions and the extensibility is found by measuring the piece used for the tensile strength before and after rupture, the time-factor may be eliminated because it is kept constant. The extensibility is then regarded as measuring the change of shape. Hence, this method combines all the three essential factors mentioned on p. 277.

In order to adapt it to indicate the potential plasticity of a clay or clay-mixture, Rosenow [2] has suggested multiplying the figure obtained by Zschokke's method by the percentage of water required to produce a mass of a consistency suitable for hand-moulding. This introduces a needless complication and it is better to make a paste of suitable consistency, determine its plasticity by Zschokke's method and report this as the potential plasticity when the necessary proportion of water (which should be stated) has been added (see p. 269).

[1] *Die Feuerfesten Thone*, 84.

[2] *Tonind. Zeit.*, **35**, 1261 (1911).

(*c*) *Compressibility Methods.*—Various methods have been suggested which are based on the amount of pressure required to effect a definite change of shape or to deform a sample of a given size to such an extent that it cracks. Thus, Stringer and Emery [1] have attempted to measure plasticity by compressing spheres of paste 2 cm. in diameter by weights placed in a pan above them until vertical cracks appear. The extent of deformation before cracking is measured by the distance through which the descending piston moves. The method does not, however, give very concordant results, nor is it satisfactory, because no account is taken of the time-factor and the change of shape is not measured with sufficient accuracy.

W. E. Emley [2] has proposed to measure plasticity by pressing upwards a block of the sample to be tested against a loose, shallow, inverted 10-degree cone by means of a spiral-screw motion. The pressure applied to the cone raises it vertically and deflects it horizontally; each of these motions causes a system of levers to move one of two suspended bobs from its original vertical position through a definite angle depending on the force applied. The plasticity is regarded as due to the average tangential force over a definite period of time, this being calculated from the formula

$$t = 9{\cdot}29 \sin a + 1{\cdot}577l \sin a,$$

where t is the tangenial force, a is the angle of deflection of the bob, and l is the distance from the point of support of the bar to the top of the bob in cm. In this case, the plasticity number depends on the size of the instrument and it is, therefore, of use only for comparative purposes. This method also takes too little account of the change in the shape of the test-piece, which is an essential factor in determining plasticity. Apart from this, it appears to be a very useful and ingenious device.

A very widely used method for estimating plasticity is one in which the change in shape is that made by immersing a small bar or needle to a definite depth into the material. A Vicat needle (p. 199), which consists of a steel rod of square cross-section, the square having the sides exactly 1 mm. in length, is very useful for this test. Those who use this method assume that the pressure required to force the needle to a definite depth into the sample in a given time is proportional to the plasticity. The pressure is applied by means of weights; the weight of the needle and weight-bearing pan must also be included. The change in shape is too small to make this method an accurate one for determining plasticity and the time-factor has been overlooked by several investigators using this method. To produce a greater change in shape, Ladd has suggested the use of a steel sphere instead of a needle and Grant has proposed to multiply the load required to sink a Vicat needle to a definite depth in the sample by the increase in area of a cylinder when compressed just sufficient to cause cracking; the latter is too indefinite to be satisfactory.

A serious objection to the use of the Vicat needle is that it confuses softness with plasticity. If the material to be tested is made into a paste of given consistency, as shown by the Vicat needle, then the plasticity is assumed to be directly proportional to the amount of water present in the sample, which is not correct.

[1] *Trans. Eng. Cer. Soc.*, **21**, 93 (1921–22).
[2] *Trans. Amer. Cer. Soc.*, **19**, 523–33 (1917).

Consequently, although Langebeck has stated that the proper consistency is obtained when the needle, under a weight of 300 grams, penetrates the sample to a depth of 4 cm. in five minutes, the proportion of water required to bring a material to this consistency cannot be used as a measure of its plasticity.

(*d*) *Shear Test.*—It has been suggested by various investigators that a shear test, in which the force required to shear a standard sample to a definite amount in a given time, would be a very convenient measure of the plasticity, but so far no method has been proposed whereby this test can be satisfactorily made. A. de Waele's method (p. 279) is really a modified shear test.

(*e*) *Various other methods*, such as P. Jachum's bending test and K. Dummel's spiral test, measure only the deformation of the material and are, therefore, not accurate, as other factors must be considered. Some methods are useless, because they are based on indefinite factors such as " toughness." The confusion in the minds of investigators is shown by a statement such as one by Stormer, to the effect that the following factors must be taken into consideration in measuring the plasticity of a substance : (*a*) absorption of water ; (*b*) binding power ; (*c*) toughness ; (*d*) adhesion ; (*e*) torsion strength ; (*f*) tensile strength ; (*g*) extensibility ; (*h*) crushing strength ; and (*i*) bending moment. Several of these may be used to measure a deforming force, but this alone is not a measure of plasticity. The amount of water which can be absorbed is also a factor of little value in this connection and there is no direct relation between the binding power and the plasticity.

Whatever method may eventually be used for determining plasticity, it must, so far as can be seen at present, be based on the three essential factors of a measurable deforming force, a measurable change in the shape of the sample and the time during which the force is applied.

Binding Power

The chief effect of water on the binding power of a clay is to increase the volume of the colloidal (gel) matter present and, therefore, to enable this matter to cover a large surface of inert material. In this way, the addition of a suitable proportion of water, acting through a sufficiently long time, will increase the actual (though only to a minor extent the potential) binding power of a plastic clay.

The binding power of a clay, as explained on p. 141, is measured by the amount of non-plastic material which can be incorporated without the plasticity of the mixture being reduced below that which is necessary for good modelling or moulding properties.

The binding power of a clay must not be confused with its plasticity, however, as these are quite distinct properties, though, as both are dependent on the nature and proportion of the colloidal gel matter present, they are, to some extent, related to one another. Thus, some highly plastic clays have a high binding power, but other clays have a high plasticity and a comparatively low binding power.

The binding power of a clay is analogous to the property possessed by various colloidal gels of retaining particles in their mass in a state of super-saturation. It appears to be due almost wholly to the viscous liquid constituent of the plastic

paste (p. 258), but the amount of non-plastic material which can be incorporated with any given clay is, of course, limited by the amount of such material already present. For this reason, any treatment which increases the proportion of viscous fluid in the mass also increases its binding power.

Clays, such as ball clays, with a high-binding power are very valuable in the manufacture of articles containing, by necessity, a large proportion of non-plastic grains, as grog bricks, porcelain, earthenware and various refractory articles of special kinds.

Atterberg has classified clays with reference to their binding power as follows :—

Class I. Clays which can be mixed with two parts by weight of sand without undue loss of plasticity.

Class II. Clays which can be mixed with only one part by weight of sand.

Class III. Clays which cannot be mixed with an equal weight of sand without being too weak to be used.

Measuring Binding Power.—The oldest method for measuring the binding power of a clay is that of Bischof, which consists in mixing the clay to be tested with a suitable non-plastic material (such as fine sand) in various proportions and with a suitable quantity of water. The mixtures are then shaped into balls of equal size, which are dried and then rubbed between the thumb and finger or with a soft brush. That mixture, which can just resist the abrasion of the fingers or brush, is regarded as showing the maximum amount of non-plastic material which can be satisfactorily added to the clay. This method gives much higher results than can be used in actual manufacture, so that some investigators have modified it by forming the mixtures into cylinders, which are allowed to stiffen slightly and are then rolled until cracks appear. The mixture which can be rolled the longest is the one which will have the highest binding power. In another modification, the greatest length to which the cylinders can be rolled without cracking is regarded as a measure of the binding power. Each of these methods lack definiteness and it is better to determine the tensile strength of the various mixtures in the pasty, dry, or burned state, as may be desired (see p. 193).

The binding power of different materials has been described more fully in connection with *Strength* (Chapter IV.).

Slips and Slurries

For some purposes, clays, clay mixtures, and other ceramic materials are used in the form of a slip or slurry, which consists of a suspension of the finer solid particles in water. Such a slip or slurry may contain almost equal weights of solid matter and water, or it may contain only 5 per cent. or even less solid matter. Owing to the large proportion of water present, slips and slurries have all the properties of fluids ; they can be poured readily from one vessel to another, can be mixed like other liquids, and have a viscosity which depends upon the nature and proportion of solid matter present.

Slips or slurries are prepared artificially (by mixing the solid materials with a suitable proportion of water) for various purposes, the most important of which are—

(*a*) To ensure a more thorough mixing of the ceramic materials than is possible when they are mixed in a dry or plastic state.

(*b*) To enable the ceramic materials to be applied more easily than would otherwise be the case, as in coating ware with an engobe or glaze or in decorating ware by painting (p. 96).

(*c*) To enable articles to be made by the process known as *casting* (*below*).

(*d*) To effect the purification of clays and other ceramic materials.

Homogeneous mixtures of ceramic materials are best prepared by mixing the dry substances in suitable proportions, soaking the mixture in water until it is thoroughly slaked, and then stirring the mixture mechanically until it is of uniform consistency throughout. An alternative method, which is usually preferred, consists in making each solid constituent into a separate slip, which is then passed through a sieve in order to separate undesirably coarse material. The consistency of each slip is then adjusted so that the slip has a definite " weight per pint " (p. 226). The slips are afterwards mixed in suitable proportions when required. This method ensures the better soaking of the solid materials and the removal of coarse matter before the proportions of the various materials are measured and so ensures the production of a superior product. If the mixed materials are required to be in the form of a paste or powder the excess of water may be removed by means of a filter-press or by driving off the water by means of heat, or by a combination of these methods. When a slip contains only a small proportion of solid matter a large part of the water may sometimes be removed by allowing the slip to " settle " for some time and then running off the clear supernatant water ; the objection to this method is that the heavier and denser particles of solid matter may settle first and so cause an undesirable amount of " unmixing."

This method of preparing pastes is largely used in the manufacture of fine earthenware, porcelain, etc., as it ensures a product of much greater homogeneity than any other method. Its chief drawbacks are its cost and the necessity of increasing the compactness of the paste by a further treatment in a pug-mill or other machine. These objections are lessened if the slips can be used for " casting " (*below*), as the filter-pressing or drying and the pugging are not then necessary.

Slips for engobes and glazes are prepared by mixing the various solid materials and water as described above, and the slip is then applied direct to the ware (see p. 96).

The slips used for making glazes and engobes are generally made up to a definite weight per pint, as this is a convenient means for measuring the amount of solid matter they contain. Thus, ball clay slips are generally of such a consistency that 1 pint weighs 24 oz., the amount of dry material being about 6½ oz. China clay slips are made up to 26 oz. per pint and contains 9–10 oz. of solid matter. Glazes usually weigh 28–32 oz. per pint. A glaze slip suitable for spraying ware should usually weigh about 27 oz. per pint.

The **casting process** consists in pouring a slip of suitable composition into a

plaster mould, in which it remains sufficiently long to enable the mould to absorb so much of the water in the slip that the mould is coated with pasty material of the desired thickness. The time required for this purpose depends on the nature of the slip. The superfluous slip is then poured away and the mould is set aside to dry, after which its contents may be removed and will be found to form an article of the desired shape.

The time required for a slip to remain in the mould before the surplus is poured off varies according to the nature of the slip. A slip made without any added electrolyte may require several hours, but if a suitable amount of alkali is added the time is considerably reduced. If ware with very thick walls is made by this process, a long time is essential even in the presence of an electrolyte. Thus, in the manufacture of gas retorts, a period of fifteen to twenty hours may be necessary. When a vacuum mould is used, as suggested by B. J. Allen, much less time is required, as the water is absorbed more rapidly by the mould.

S. R. Hind [1] found that the thickness of the cast clay produced in a plaster mould which is not more than half saturated is approximately expressed by the formula

$$l^2=200x_0r_0t(1-s^2),$$

where l is the thickness of the cast in mm., in the time t hours, x_0 the rate of passage of water through 1 cm. cube of casting on to a dry mould in c.c. per hour, r_0 the ratio of volume of casting : volume of water removed, and s is the ratio of the water in mould : water required to saturate mould.

The nature of the clay or other ceramic materials affects the properties of the slip used for casting, especially when this process is used in the manufacture of articles from materials which, by themselves, are insufficiently plastic to be moulded into shape, as is the case with porcelain and with some of the feebly plastic mixtures of clay and grog used for crucibles, glass-melting pots, retorts, etc. Thus, china clay and kaolins produce a very porous product when cast, but they have not sufficient binding power to produce a strong mass. Ball clays, on the other hand, have the requisite binding power, but give too dense a product, which makes it very difficult to secure the formation of a sufficiently thick layer in the mould. Fireclays vary in their properties in accordance with their nature, but are usually intermediate between kaolins and ball clays.

To secure the best results in casting, it is necessary to use a suitable combination of clays so as to produce a moderately plastic material of sufficiently binding power. Slightly plastic materials are preferable to highly plastic ones in casting, as they require less alkali to maintain a suitable fluidity and the articles can be more readily removed from the moulds. For this reason, finely ground burned clay (grog) is often used in place of some of the raw clay. Rohland [2] has stated that the greater the amount of organic colloid matter in a clay the more susceptible is the clay to the action of alkalies and, therefore, the more suitable is it for casting. This does not appear to apply to organic matter added purposely to a clay.

[1] *Trans. Eng. Cer. Soc.*, **22**, 90 (1922–23).
[2] *Sprechsaal*, **42**, 1 (1909).

The proportion of water in a slip used for casting should be as small as possible so as to avoid undue shrinkage of the ware. In estimating the amount of water required, it is necessary to use only dry materials or to take into account the moisture contained in the raw materials. The amount of water used also depends upon the amount of deflocculant used. If no deflocculant is used, most dry clays will require almost an equal weight of water to convert them into a slip, but with a deflocculant good slips may usually be produced which contain only about 20–25 per cent. of water. Non-plastic materials may usually be made into dense slips ; thus, slips for casting zirconia crucibles may weigh about 30 oz. per pint. It is most important that the correct consistency should be obtained, as too thick a casting slip may cause discoloration and staining, even when it produces sound articles. The risk of producing defective articles by the use of too thick a slip is often serious.

If a suitable slip is used, this method of manufacture requires very little skill, and yet it enables articles of complex shape and with extremely thin walls to be produced from materials of low plasticity. It is, therefore, a very valuable method for the manufacture of fine earthenware porcelain, etc. In recent years, it has also been used for the manufacture of large articles, such as pots for melting glass, large crucibles, retorts, and sanitary ware, in all of which a highly homogeneous material is required.

If plain water is used, a very large proportion of it will be required, and this will result in a large contraction when the contents of the mould are dried. To avoid this, and the resultant risk of distorting the ware, it is desirable to use as little water as is consistent with the necessary fluidity of the slip, or to make use of the colloidal properties of many ceramic materials. In order to use a smaller proportion of water than would otherwise be required, instead of plain water, a very dilute solution of sodium carbonate or other suitable electrolyte is used, because, as previously explained (p. 246), clays can be deflocculated and rendered more fluid by adding alkalies, etc. Thus, the addition of about 0·25 per cent. of sodium silicate or of soda ash, or a mixture of these two substances, will increase the mobility of a slip weighing about 36 oz. per pint to that of an untreated slip weighing only 26 oz. per pint.

Various deflocculants for clay have been described on p. 247, but all are not equally suitable. Sodium carbonate or sodium silicate, or a mixture of these two, are usually the most satisfactory, but when sodium carbonate alone is used a high-surface tension is produced and the solid particles tend to " ball up " and cause the entanglement of air bubbles. Sodium silicate alone, on the other hand, tends to produce a " stringy " slip and it does not hold the clay in suspension so well as sodium carbonate. If only a single electrolyte can be used, sodium carbonate appears to be the best. Sodium hydrate is much more active than sodium carbonate and silicate, but it is not used to any great extent, partly because of its corrosiveness.

An excess of electrolytes is very undesirable and should be carefully avoided, as it may have a flocculating effect. If a clay or other material which it is proposed to convert into a slip contains soluble coagulating salts, they may interfere by increasing the viscosity of the slip. Thus, the presence of 0·002 per cent. of calcium sulphate may prevent a clay being made into a suitable slip. Consequently, when such

substances are present, a suitable precipitant, such as barium hydrate, should be added prior to the addition of the deflocculating salt.

The proportion of deflocculant which is the most suitable for any given purpose must, of course, be found by trial. The effect of electrolytes on a ceramic slip may be determined by churning together definite quantities of the clay or other solid material and water with different proportions of various electrolytes for a period of about two hours. The resultant mixture is allowed to remain at rest for a suitable time and is then examined. The resulting slip which most closely corresponds with what is required is then noted. In making slips of various materials it is most important that they should be added to the required amount of water in the following order: (*a*) deflocculating salts (if any); (*b*) clays; (*c*) non-plastic materials. This procedure is necessary, because when all the materials are added at once an excessive quantity of water is required. When sulphates are present, the clay and sufficient water should first be mixed, the requisite amount of barium hydrate or other precipitant added, and this mixture then added to the remainder of the water in which the deflocculating salt (sodium carbonate, etc.) has previously been dissolved.

Schory [1] found that the lowest viscosity is obtained by preparing the slip in the following manner: (i) Add the deflocculating salt (sodium carbonate) to the water; (ii) then add the solid materials; (iii) finally add the sodium silicate. According to him, a slip made in this way had a viscosity of 2·72, whereas when the carbonate and silicate were added together before the solid materials, the viscosity was 5·21. When the silicate was added first and the carbonate last the viscosity was 4·60.

Wright and Fuller,[2] on the contrary, suggest the following order in making the casting slips: dissolve the silicate in the water, add the dry materials, mix thoroughly, then add the sodium carbonate and complete the mixing.

In all cases, very thorough mixing is necessary to secure homogeneous slips, a day or more being sometimes necessary to secure uniformity.

Many of the experiments made on the effect of various substances on the viscosity and other properties of casting slips appear to have been made without sufficient recognition of the many factors involved. To understand what may be taking place it is necessary to bear in mind (as pointed out by M. H. Fischer in another connection) the effects of (*a*) the quantitative relationships of the water-content of the system to the remaining material; (*b*) the chemical conversion of "neutral" compounds into basic or acidic derivatives; (*c*) the alterations in solubility and hydration-capacity accompanying the reaction; (*d*) the types of system produced (whether all hydrated colloid, all solution in water, a mixture of colloid and non-colloid, or subdivisions of any of these); and (*e*) the changes in viscosity incident to the "emulsification" or "suspension" of any of the unchanged "clay" in such derivatives as may be produced. How inadequate for the understanding of the colloid-chemical behaviour of such systems are the usual ideas of "stoichiometry," "chemical affinity," "electrical charges," "hydrogen and hydroxyl ions," which are usually regarded as exclusively explaining them, is self-evident.

[1] *J. Amer. Cer. Soc.*, **3**, 290 (1920).
[2] *Ibid.*, **2**, 659 (1919).

The experimental observations may be correct, but the whole problem involves inquiry into still more fundamental ones on the nature of solution which at present are unsolved. We must, for the moment, be content to realise that no single property explains all these phenomena and no law correlating them all has yet been discovered.

The temperature of casting is very important, as variations in temperature may cause changes in the viscosity of the slip. The change in viscosity with the temperature is not regular; in many cases, there is a point of maximum viscosity at a relatively low temperature, there being a sudden increase in viscosity as the temperature passes through a critical point, followed by an equally sudden fall as the temperature rises still higher. Weber has utilised this property in the manufacture of glass-melting pots. He carefully ascertained the temperature and proportion of electrolytes necessary to obtain a slip of maximum fluidity and concentration and used this for casting. The requisite increase in temperature is so slight that it can usually be produced by vigorously stirring the slip in a mechanical agitator or ark. A few minutes after the slip has entered the mould the withdrawal of a little of the contained water through its absorption in the pores of the mould suffices to effect the gelation of the remaining colloid and further storage then produces an effective casting of any desired thickness.

There are various other factors involved in slip casting which are not dependent entirely on the nature of the clay. According to S. R. Hind,[1] the following are the chief of these :—

1. The time required to give the required thickness of deposit.
2. Alteration of the nature of the slip during casting.
3. The proportion of water in the cast clay on the mould after casting.
4. The porosity of the mould.
5. The degree of saturation of the mould.
6. The resistance of cast clay to the passage of water.

Purification of Clay.—As the ultimate particles into which clay can be separated by water are much smaller than those of most of the impurities commonly present in clays and allied materials, a considerable amount of purification may be effected by making the crude material into a very dilute slip, allowing the latter to remain at rest for a suitable time and then running off the supernatant liquid. During the period of rest, the greater part of the impurities will settle, whilst the clay particles, together with the smaller particles of impurities, will remain in suspension and so can be run off with the water. An elutriation process (p. 50) may also be used.

If plain water is used, the slip must not usually contain more than about 20 per cent. of solid matter, and where a high degree of purification is required, the slip should not contain more than about 5 per cent. of suspended matter. These dilute suspensions consequently involve the use of very large quantities of water and prolonged periods of settlement and are, therefore, troublesome and often costly. That they are effective is shown by the high quality of china clay obtained by elutriation

[1] *Loc. cit.*, p. 284.

in Cornwall from a decomposed granite which usually contains less than 50 per cent. of china clay.

Considerable commercial and technical advantages may be secured by making use of the colloidal properties possessed by clays, by means of which they can be suspended in a much smaller proportion of water and yet effectively separated from other (non-colloidal) materials which cannot be so readily suspended.

To effect the purification of clays by this means, use is made of the fact that clays, like colloidal materials, can be dispersed (see p. 246) by means of a suitable agent, and when so dispersed or deflocculated they remain permanently in suspension until their state is changed by the addition of a coagulant or flocculating agent. Hence, whilst clay readily enters into suspension in the presence of a suitable proportion of alkali or other suitable deflocculating agent, the principal impurities found in clay, such as quartz, mica, felspar, pyrites, calcium carbonate, and various iron compounds, are not affected. Consequently, when stirred well with alkaline water, they only remain suspended for a short time and soon settle out, so that the purified clay suspended in water may readily be removed. Any of the deflocculating agents mentioned on p. 247 may be used, though some are more convenient than others. Various patents have been taken out for the use of special deflocculating agents; thus, W. Feldenheimer [1] uses "sesquicarbonate of sodium," ammonium carbonate, or potassium carbonate and recommends the first as superior to the others. Bleininger [2] prefers caustic soda, or a mixture of caustic soda and water-glass in equal parts. G. H. Brown and W. L. Howat,[3] and I. E. Sproat,[4] have also recommended caustic soda.

The amount of alkali or other peptising agent depends upon the clay and must be found by trial. It is, in all cases, a very small percentage of the total weight of the clay; usually less than 1 lb. per ton.

Feldenheimer has recommended the use of 8·8–126·6 parts of sodium sesquicarbonate or 23·5–78·5 parts of ammonium carbonate or 9·6–69 parts of potassium carbonate in 1000 parts of water for suspending 500 parts of clay. These are much larger proportions than have been found by the author to be desirable to obtain the most efficient purification and the author's investigations agree more closely with those of G. H. Brown and W. L. Howat, who use 0·05–0·25 per cent. of caustic soda.

Very simple stirring appliances suffice for the suspension of the crude materials and only plain tanks are required for containing the liquid during sedimentation and for receiving the purified clay in suspension. If sufficient care is taken to add a suitable proportion of deflocculant, the separation of the clay from the greater part of the impurities is fairly sharp, though some impurities—chiefly soluble salts and extremely small particles of silica and various iron compounds—cannot be completely separated. The chief difficulties connected with the process are found when it is required to separate the purified clay from the water in which it is suspended. To effect this, four general methods are available :—

(*a*) *Removal of the water by evaporation*, usually by the aid of heat. This is very

[1] *Eng. Pat.*, 108, 808 (1916).
[2] *J. Franklin Inst.*, **180**, 225–7 (1915).
[3] *Trans. Amer. Cer. Soc.*, **17**, 81 (1915).
[4] *Ibid.*, **18**, 767 (1916).

effective, but usually too costly. It also causes any soluble salts in the water to remain in the clay. Where waste heat is available, this method is still worth consideration. If this method is used, care must be taken not to over-heat the clay or its active properties may be destroyed.

(*b*) *Filter-pressing*, see p. 294.

(*c*) *Flocculation* or precipitation of the suspended clay particles by the addition of acids or other electro-negatively charged substances (p. 243). Any of the flocculants mentioned on p. 244 may be used, though the most convenient are hydrochloric acid, acetic acid, aluminium sulphate, or aluminium chloride. Sulphuric acid has also been used for this purpose, but it has the serious disadvantage that, when the clay is afterwards dried by artificial heat, the sulphuric acid chars any organic matter present and so spoils the appearance of the clay. The only disadvantage of the use of a flocculant is that any colloidal impurities present or any impurities which may be adsorbed will contaminate the clay.

(*d*) *Electro-osmosis* (p. 249), *i.e.* by the use of a current of electricity to separate the water and suspended matter. This is an excellent method, as it can simultaneously effect a further slight purification, especially from iron compounds, but it is very costly. The general phenomena of electro-osmosis and the accompanying kataphoresis have been dealt with in respect to colloids generally on p. 229. When it is employed for separating clays from their suspension in water, the apparatus used consists of a tank containing in the lower part two paddles which serve to keep the suspension in agitation and direct it in a stream through the numerous small spaces in the cathode fixed immediately above and which surrounds the lower half of the anode. The anode consists of a metal cylinder, revolving at a speed of about one revolution in three minutes, at a distance of about $\frac{3}{4}$ inch from the cathode. A scraper removes the clay from the anode, whence it falls down a chute clear of the machine. A fresh clay suspension is fed into the lower part of the container and the water effluent returns to be mixed with fresh clay. The manner in which the machine acts towards the clay is as follows: the clay in suspension, in passing through the laminated or perforated cathode, becomes negatively charged and is immediately attracted to the anode cylinder, the water being driven towards the cathode. There is thus formed a drier layer of clay on the anode cylinder and a wet zone of clay suspension round the cathode. Fresh clay entering the machine encounters the watery zone on its passage to the anode, in which zone the electro-osmotically indifferent particles, such as pyrites, mica, and quartz, become freed from the clay and are either deposited on the bottom of the tank or are washed away.

The clay leaves the machine in the form of a blanket from $\frac{1}{4}$ to $\frac{1}{2}$ inch in thickness containing only about 25 per cent. of water. If a drier product is required, the remaining water must be removed by evaporation.

Various statements have been made from time to time to the effect that crude clays may be purified by electro-osmosis. This is scarcely correct, because the electro-osmosis does not, in itself, effect the chief separation of the impurities from clay, but only separates much of the water. The most important impurities, such as quartz, mica, felspar, etc., bear the same electric charge as the clay particles and so cannot

be separated, though oppositely-charged impurities, as free iron oxide, may be separated by electro-osmosis. When iron oxide is adsorbed by clay, it does not act in an electrically opposite manner to the clay when the mixture is subjected to the action of an electric current, and, consequently, adsorbed iron oxide cannot be readily separated from clay by this method. Even free iron oxide is only attracted to the cathode when a strongly adsorbed cation is present in the liquid so as to neutralise the effects of hydroxyl ions.

The greater part of the impurities is separated by deflocculation and settlement (p. 288) before the material enters the osmose-machine, and the latter is more correctly to be regarded as a drying device.

Properties of Slips.—The most important properties of ceramic slips, and especially those containing clay, are :—

(i) *Their behaviour as suspensions*, as a result of which they can form a pasty deposit on any porous material inserted in them or containing them. This property is made use of in casting (p. 283) and in engobing or glazing (p. 96) ware. The water is absorbed by the mould or article to be covered and the solid matter is then deposited. Clay slips possess many of the properties of colloidal sols (p. 228) and, like them, may be coagulated or flocculated by the addition of acids (p. 243).

(ii) Their *viscosity* is usually important, as it regulates, to some extent, their behaviour when used for casting, glazing, etc. The viscosity appears to be largely (though not wholly) dependent on their colloidal properties, as clay slips are similar to emulsoids in that they increase in viscosity with greater concentrations, but they resemble suspensoids and differ from many emulsoids in being easily flocculated by electrolytes.

Suspensions of clay containing up to 3 per cent. of solid matter have, according to Bleininger, a lower viscosity than that of water. He suggested that this may be a result of the deflocculation of the clay and the solution of the electrolytes present. With greater additions, when the proportion of clay present is in excess of that required to produce a colloidal sol, the viscosity is increased.

Viscosity may be defined as the resistance to flow offered by a fluid and it is, therefore, the converse of fluidity or mobility. It is usually expressed in terms of the quantity of material which will flow through a given orifice in unit time, but may also be expressed in other ways. Most of the viscosimeters commonly used do not permit the viscosity to be expressed in terms of absolute units, though this is in every way preferable.

The viscosity of a clay slip is greatly affected by the presence of minute proportions of flocculants (p. 243) or deflocculants (p. 246). Thus, H. E. Davies [1] found that the addition of up to 0·1 per cent. of tannic acid increased the viscosity of clay slips ; the addition of 0·1–0·4 per cent. decreased the viscosity ; if a larger proportion is added, the viscosity is again increased. If 0·3 per cent. of tannic acid is present, the slip will have approximately the same viscosity as that to which no addition has been made.

Measurement of Viscosity.—A very convenient apparatus devised by A. de Waele is shown in fig. 16. The short limb of the U-tube consists of a capillary of

[1] *J. Amer. Cer. Soc.*, **5**, 702 (1922).

dimensions suitable to the liquid under examination, cemented by means of molten shellac to the other limb, terminating in a stop-cock or clip. At a point above the capillary a cork carrying a pin point downwards is passed, this pin serving as an indicator. The U-tube is filled with the liquid under examination through the cock, the latter closed and the capillary end of the U-tube then immersed in the liquid to be tested contained in a boiling tube maintained in a thermostat, the position of the U-tube being adjusted so that the pin-point dips below the surface of the liquid. The

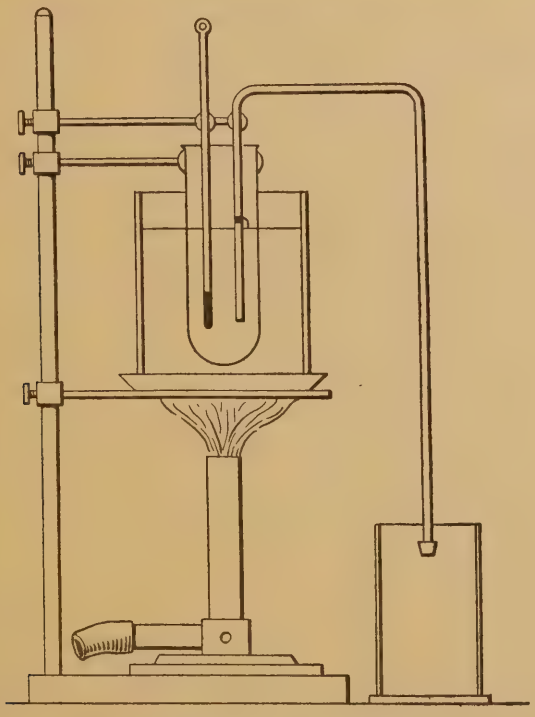


FIG. 16.—VISCOSITY APPARATUS.

cock is then opened and, at the moment when the liquid in the boiling tube just passes the point of the pin, a receiver is placed under the liquid issuing from the other limb, a stop-watch being started simultaneously. A constant head is maintained by raising the boiling tube so that the surface of the liquid therein is as close as possible to the pin point. After a definite interval of time, or when sufficient liquid is judged to have passed over, the cock is closed, the stop-watch arrested, and the volume of liquid measured from its weight and density.

$$n = \frac{g^2 R^4 t p H}{8 l Q},$$

where n is the viscosity coefficient, g the gravity constant (981), p the density of the liquid, H the vertical height from the point of the pin to the outlet, R the radius of

the capillary, l its length, and Q the volume of slip passing through the capillary during the time t.

Where only comparative results are required the viscosity of clay slips may be determined by measuring the rate of flow through a 2 mm. aperture under a constant pressure.[1] The coefficient of viscosity when using this method is

$$\frac{\text{Volume of liquid discharged in a given time}}{\text{Pressure of the liquid}}.$$

Viscosity may also be calculated from the following formula :—

$$V = S \times \frac{Ts}{Tw},$$

where V is the viscosity of the slip, S is the specific gravity of the slip, Ts the time required for 250 c.c. of slip at 18° C. to flow through the orifice, and Tw the time required for 250 c.c. of water at 18° C. to flow through the orifice.

Simonis also measured the viscosity of thick clay slips by determining the weight required to pull a 5 cm. glass plate from the surface of the slip, the viscosity being expressed as the relation between this and the weight required when water was used. The chief difficulty of this method is in the variations which occur if any settling of the suspended matter in the slip takes place.

Bleininger [2] measured the viscosity by suspending a disc weighing 1333 grams by means of a wire 11 ft. 6 in. long and 0·85 mm. diameter in a tank containing the slip to be tested. The disc is turned through an angle of 180° and released, and the amplitude of the swing measured several times. The ratio between two consecutive amplitudes of swing is constant for the same slip at the same temperature. The viscosity may be calculated by the following formula :—

$$K = \frac{T_2 \log . r_1}{T_1 \log . r_2},$$

where T_1 and T_2 are the periods of oscillation in water and the slip respectively, whilst r_1 and r_2 are the ratios of the amplitudes of any two consecutive swings in the same direction in the same liquid at the same temperature.

A. V. Bleininger and G. H. Brown [3] measured the viscosity of clay slips by determining the time taken for a paddle-wheel, driven by means of a descending weight of 200 grams, to revolve 100 times when immersed in the slip. The relative time taken, compared with the time taken when the paddle revolves in the air and in water, is a measure of the viscosity. Thus, if the time taken in air is 3 seconds, in water 12 seconds, and in the slip 21 seconds, the viscosity is

$$\frac{21 - 3}{12 - 3} = 2{\cdot}0.$$

[1] Simonis, *Sprechsaal*, 597 (1905).
[2] *Trans. Amer. Cer. Soc.*, **10**, 389 (1908).
[3] *Ibid.*, **11**, 596 (1909).

W. E. Emley's viscosimeter [1] is somewhat similar and consists of a hollow cylindrical paddle which is rotated by electro-magnetic means in the tank containing the slip. The speed of rotation is measured by an optical device and compared with the speed of rotation in water, the comparison giving the relative viscosity of the liquid to that of water.

The viscosimeter devised by H. H. Clark [2] consists of a paddle which is deflected in a square tank containing the liquid to be tested by means of a rotating electro-magnet, the amount of deflection, with a definite current and speed, varying with the viscosity of the liquid. The current in the electro-magnet is increased until the paddle revolves at a definite speed and the viscosity is calculated by estimating the torque of the paddle, in gram-centimetres, from the results of a previous calibration of the instrument.

The author prefers an efflux viscosimeter such as that shown in fig. 16 or of the well-known Ostwald pattern, as the results are obtained more simply and, on the whole, more accurately than those of paddle-viscosimeters.

[1] *Trans. Amer. Cer. Soc.*, **15**, 450 (1913).
[2] *Ibid.*, **12**, 375 (1910).

CHAPTER VII

CHANGES IN THE PHYSICAL STATE FOLLOWING THE REMOVAL OF WATER

The removal of water may be effected in various ways, of which the most important are—

(*a*) *Evaporation* or *Drying.*
(*b*) *Filtration,* more especially by means of filter presses.
(*c*) *Sedimentation* or *Settlement.*
(*d*) *Electro-osmosis* (p. 289).

The complete removal of water can only be effected by the first of these methods ; the others produce a paste which may contain 16 per cent. or more water.

Drying is effected by (*a*) exposing the material to a quantity of either cold or warm air which is sufficient to absorb and carry off the water, thus leaving the clay in a dry or almost dry state ; (*b*) heating the material so as to convert the water into steam, which then escapes into the atmosphere. The method which is most appropriate in any particular case must depend on the nature of the material or article to be dried and upon the state of the water present. If a ceramic material consists of a slip or very soft paste it may be cheaper to effect a partial separation of the water by means of a filter press and to complete the separation by drying the product. Solid or pasty materials must usually be dried if it is required to separate the water present in them.

Removal of Water from Slips.—In a slip (p. 282) the water usually constitutes the bulk of the material, the particles of solid matter being suspended in it. When such a slip is placed in a porous vessel, such as a plaster mould or the bag of a filter press, the greater part of the water passes through the pores of the vessel and so is separated from the solid particles, most of which are too large to enter the pores. If an extremely fine suspension (such as a colloidal sol, p. 11) is treated in this manner, the particles may be small enough to pass through the pores, and consequently no separation of them from the water will be effected.

The removal of water from a slip in the manner indicated is clearly a mode of filtration, the small particles of water passing through the pores of a filter which are too small to permit the passage of the solid suspended particles.

When a slip is allowed to remain quiescent for a sufficient time, many of the suspended particles will settle and some of the clear water may then be run off, or

decanted and so separated. Finally, the whole of the water in a slip may be removed by the application of heat, which converts the water into steam, but this method is usually too costly to be applied to slips without subjecting them to one of the other methods just mentioned in order to reduce the amount of water present.

Removal of Water from Pastes.—In a paste the water may be present in one or more of three forms : (*a*) a superficial film surrounding each solid particle ; (*b*) as interstitial water, *i.e.* as water occupying the pores or interstices between the solid particles so that each solid grain is separated from every other by a superficial film of water and by the interstitial water ; or (*c*) the water may be absorbed into the colloidal material coating the grains, causing the colloidal matter to swell like soaked glue and each solid particle to be separated from every other by the colloidal gel.

Only the interstitial water can be removed from a paste by mechanical means such as by subjecting the mass to great pressure, and even then the removal is incomplete, so that the only effective method of removing water from a paste is by some mode of drying. When the water is gradually withdrawn from a paste in this manner, each form in which it occurs is the cause of certain physical changes in the material, and the drying therefore appears to occur in several distinct stages, though these overlap to some extent.

The drying may be effected (*a*) by cold or warm air ; (*b*) by heat applied to the mass by convection or by radiation (Chapter XII), or (*c*) by means of a dehydrating or desiccating agent, such as sulphuric acid, which absorbs moisture from the atmosphere surrounding the material to be dried.

In the **first stage** some of the interstitial water is removed, with the result that the solid particles draw closer together and the mass as a whole contracts or shrinks. At the end of this first stage, the solid gel particles still remain covered with a film of colloidal gel, and some of the less markedly colloidal particles may remain covered with an adherent film of water. The contraction of the mass in this first stage of drying is dependent, to a large extent, on the amount of water used in preparing the paste, as this determines the extent to which the particles are separated from each other and the amount of compacting which is possible when such interstitial water is removed. Thus, articles which are cast undergo a far greater contraction in drying than moulded articles, on account of the larger proportion of water used in making the slip and in the development of its colloidal properties.

In the **second stage** of drying, the film of water surrounding the non-colloidal particles is removed and a further slight shrinkage occurs as the solid particles draw still closer to each other. At the end of this stage, the solid particles (including those surrounded by a gel) are in direct contact with each other, though they do not touch at every part, and, consequently, there are voids, pores, or interstices between them.

In the **third stage** of drying, the water in the colloidal gel is removed, so that a still further shrinkage of the mass occurs and the particles draw still closer together. For this reason, the contraction which some clays undergo on drying increases with the colloidal content of the clay. Hence, the drying of a clay paste is partly a colloidal phenomenon and partly the result of the evaporation of water from the pores in the mass.

Plastic clays and clays rich in colloidal matter shrink more than lean ones, but there is no definite relation between the plasticity and contraction of a clay, as the latter property is dependent on a number of factors other than the plasticity of the mass. The water lost during these stages of drying may be termed *shrinkage water*; when the whole of this has been driven off, the solid particles composing the mass will be in contact with one another and no further shrinkage or drying can occur.

The removal of the shrinkage water from articles composed of plastic clay is often difficult, because, unless it is effected in a suitable manner, serious cracking and distortion of the articles may occur. This risk may be reduced—

(*a*) By making the articles of a much stiffer paste.

(*b*) By the use of non-plastic material in the substance of which the articles are made, as such non-plastic materials do not shrink seriously when dried. Thus, pastes made wholly of ball clay shrink very greatly when dried, the linear contraction often exceeding 2 inches per foot. China clay has a much smaller contraction, and when added to a ball clay will reduce the drying-shrinkage of the latter. Similarly, a mixture of ball clay with flint, felspar, or other non-plastic material may have so low a shrinkage that articles made of it can be dried without serious risk.

(*c*) By drying the ware so slowly or under such carefully controlled hygrometric conditions that the risk of distortion or cracking is reduced to a minimum.

Other factors influencing contraction include—

(*a*) The *fineness and shape of the grains*, as these determine, to some extent, the amount of water required to cover the grains, the volume of the interstices between them, and the extent to which they will slide together during the removal of the shrinkage water. This is particularly the case with grains which are so minute that they possess colloidal properties.

(*b*) The *rate of drying*, for if a ceramic article is dried rapidly the particles will not be able to move over each other so freely as when dried slowly; consequently, the shrinkage is less, the ware is more porous owing to the grains not being arranged so compactly, and the internal strains are greater and may be serious.

The greatest permissible rate of drying depends principally on the permeability of the mass. If many of the pores are large, the water can readily escape from them, but a material containing very minute pores must be dried much more slowly or the pressure of the water vapour in the pores will cause the mass to crack. Thus, a lean clay, such as china clay, may safely be dried more rapidly than a highly plastic clay, although both may contain the same amount of water, because the former is more porous. Unless the drying is excessively rapid, it occurs almost exclusively at the outer surface of the material, and as the pores nearest this surface are dried more water reaches them from the interior to take its place, this action continuing until all the water has been removed. Consequently, under normal conditions of drying, the water escapes as fast as the capillary action is able to transmit water through the pores to the surface. If, on the contrary, the heat applied to the material is such that some of the water in the pores is converted into vapour more rapidly than it can escape to the surface, the pressure produced may cause the mass to crack and necessitate a slower rate of drying in future.

(c) *Irregular or Uneven Drying.*—One part of the mass being dried more rapidly than another. Even under the most carefully regulated conditions, the contraction does not proceed regularly during the removal of the water, nor does it continue until no water is left in the mass ; it almost ceases as soon as the solid particles come into close contact with one another, though a very slight further contraction must occur when the water is driven out of any matter which may be present in the form of a colloidal gel.

The **fourth stage** of drying occurs when the solid particles are in close contact with each other, but the interstices between the grains (due to their irregularity in shape) are full of water. At the commencement of this stage, the water remaining in the clay or other material is wholly contained in the pores of the mass and, consequently, it can be removed without any further change taking place in the volume

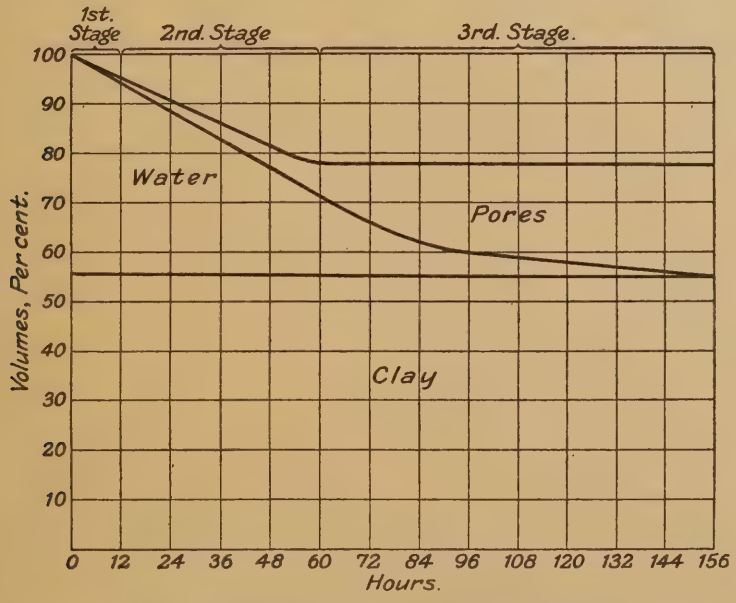


Fig. 17.—Changes in Volume during Drying.

of the material. For this reason, there is little or no danger of cracking, and the drying may usually be completed as rapidly as is desired.

The rate at which the contraction (or change in volume) occurs as compared with the rate at which the water is removed is shown in fig. 17, in which it will be seen that the shrinkage is fairly rapid at first, but gradually slows down and ceases when 8 per cent. of water is still present in the material.

Dry clay is a porous material in which many of the pores are too small to be visible, even under the most powerful microscope. The walls forming the pores must be continuous to account for the cohesion of the clay, but the pores must communicate very completely on account of the ease with which fluids are absorbed.

Probably the best conception of a mass of dry clay is that which compares it to a sponge or honeycomb with perforated cell-walls.

Dried pastes are hard because, when the water has been driven off, the solid particles are no longer covered with a thin film of water or soft gel, nor are they separated by a further quantity of water; each of these, when present, acts as a lubricant, which enables the particles to move readily over each other when the mass is subjected to pressure, but in their absence the particles are in contact with one another and the friction between them is then so great as to prevent their moving, except under a destructive force, and the mass becomes *hard*. The plasticity is reduced as the thickness of the aqueous film or gel diminishes, and when all the water has evaporated the mass is wholly devoid of actual plasticity, though, if the clay present has only been dried and not decomposed, it may still possess great potential plasticity and can be reconverted into a plastic mass by mixing it with a suitable proportion of water.

Hygroscopicity.—When a clay is dried cautiously so as to avoid more than a negligible amount of decomposition, the product is hygroscopic, *i.e.* it can absorb water slowly when it is exposed to moist air, but under normal atmospheric conditions the proportion so absorbed is far less than would be required to make the material plastic.

CHAPTER VIII

CHEMICAL CONSTITUTION OF CERAMIC MATERIALS

ALL matter is composed of certain fundamental substances termed *elements*, which have not, as yet, been decomposed into simpler substances by any known chemical process. Eighty-seven elements are known, but recent investigations of the spectra produced by X-rays have shown that there are apparently ninety-two different elements. Some bodies known as elements yield compound X-ray spectra, showing that they consist of two or even more substances, though these " isotopes " are so similar in their action that they have not been isolated. Of the elements used in substances which are employed in the ceramic industries, hydrogen, carbon, nitrogen, oxygen, fluorine, sodium, phosphorus, sulphur, arsenic, and iodine are, according to F. W. Aston, simple elements; but boron, chlorine, potassium, nickel, bromine, uranium, and possibly calcium, consist of two fundamental substances. Magnesium consists of three, and silica may consist of either two or three, the number at present being a little doubtful. Zinc may consist of four and mercury of six fundamental substances.

Although these fundamental substances (termed *isotopes*) exist and at some future time may be isolated, it is convenient at present to regard what are usually known as elements as simple substances, because the constituent isotopes of the complex elements act in an exactly similar chemical manner to the element taken as a whole. An element may, therefore, be defined as a substance with a unique X-ray spectrum; it may or may not be a mixture of isotopes, but it cannot be decomposed into anything simpler by any known chemical process.

Elements are classified into metals and non-metals, according to their characteristic properties. In the ceramic industries, elements, as such, are not extensively used; their importance lies in their influence as constituents of the various " compounds " employed. Thus, the non-metal *silicon* is not used in its elementary form in ceramics, but, in combination with oxygen (when it forms the compound *silica*), it is one of the most important ceramic substances. Similarly, the metallic element aluminium is little used in the ceramic industries, but its oxygen-compound, alumina, is of great importance. Some compounds may combine with other compounds, forming such complex substances as clay, which may be regarded as a compound of the compounds silica, alumina, and water, these being composed of the elements silicon and oxygen, aluminium and oxygen, and hydrogen and oxygen respectively. The arrangement of the elements in a compound is described on p. 302.

A chemical compound differs from a mixture of the same substances in various

ways : (*a*) A mixture of two or more substances has properties which are the mean of those of its constituents. The properties of a compound are usually widely different from those of its constituents. (*b*) In a mixture, the relative proportions of the constituents may be varied at will, but those in a pure compound are constant. (*c*) The various constituents of a mixture may be separated by mechanical or physical means, but the constituents of a compound cannot be so separated. (*d*) During the formation or decomposition of a compound a change in temperature usually occurs ; this is not the case with a mixture.

Most natural clays are mixtures of various chemical compounds which can be separated by mechanical means. Thus, by stirring a clay with a sufficient quantity of water and then allowing it to rest, the clayey portions may remain in suspension whilst the sand and heavy minerals separate out. A more refined mechanical treatment of the suspended and deposited matter respectively will enable other substances to be separated, until eventually all the constituents are isolated.

Limestone, magnesite, silica, kaolinite, carborundum, alumina, etc., on the contrary, are each, *when pure*, definite, chemical compounds, the constituents of which are so united that they can only be separated by heat or chemical action.

Intermediate between a "mixture" and a "chemical compound" are *solid solutions*, the properties of which are partly those of a chemical compound and partly those of a mixture. Solid solutions are very important in the ceramic industries, as this is the state of many of the final products formed during the various manufacturing processes ; they are described in Chapter XI.

There is no definite dividing line between mixtures, solid solutions, and chemical compounds ; each may pass imperceptibly into another, some substances appearing to be on the border-line between two phases. Liquid solutions also appear to be intermediate between chemical compounds and mixtures, for though the affinity of the solvent for the dissolved substance is weak, it is not entirely absent, and most solutions are more than mere mixtures.

Atoms and Molecules.—All matter consists of an aggregation of particles, the smallest particle which can exist as a separate entity, and yet preserve the properties of the mass, being termed a *molecule*.

A molecule may be regarded as a miniature Jupiter with its satellites or moons, each revolving round the central mass.

The plane graphic formulæ (p. 308) commonly used are deficient, inasmuch as they only represent two out of the three dimensions of the molecule.

Neumann and Joule's observations suggest that the constituent atoms of a solid compound behave as if the solid were a mechanical mixture of the component atoms, each atom being free to vibrate independently of the rest.

Molecules are in a state of violent and perpetual motion, otherwise, gases and liquids could not diffuse. Hydrogen molecules have a velocity of 184,100 cm. per second, or 70 miles per minute, but carbon dioxide molecules only one-fifth of this speed. Molecules are supposed to be perfectly elastic, so that after each collision they rebound with the same velocity as before. A molecule of hydrogen undergoes 10,000,000,000 collisions per second, but a carbon dioxide molecule or water molecule only

6,500,000,000 collisions per second. Molecules of solids move far less rapidly than those of liquids, their rate of motion increasing with the temperature.

A molecule may be decomposed into its constituents termed *atoms*, which are composed of elements (p. 299).

For many years the atom (as its name implies) was regarded as indivisible, but recent investigations have shown that the atoms of different elements have the same general type of structure, and that at the centre of each atom is a positively-charged nucleus (or proton) of minute dimensions (in heavy atoms not more than $\frac{1}{5000}$ of the diameter of the whole atom, and in lighter atoms even less than this fraction), in which the greater part of the mass of the atom resides. This nucleus is surrounded by a number of electrons (held in equilibrium by the nuclear forces) as the planets surround the sun in the solar system. By the action of light and electrical discharges, one or more of the external planetary electrons may be separated from the atom, while by the action of other fast-moving rays it is possible to detach one of the more strongly-bound electrons from the atomic structure. It is now agreed that the complex nuclei of all atoms are built up of hydrogen- and helium-nuclei and electrons, while the helium nucleus itself is composed of four H-nuclei and two electrons. Probably the nuclei of all atoms are composed of positively-charged H-nuclei or "protons" with the addition of negatively-charged electrons.

As a proof of these remarkable assertions, nitrogen, fluorine, phosphorus, and aluminium, when bombarded with the X-rays from one of the radium-group of elements, yield hydrogen atoms, liberated from the nuclei of these elements. It is probable that the H-nuclei are satellites of the main nuclei of these elements. Nitrogen, for example, has been split up into helium and hydrogen, this element being composed of three nuclei of He (each of mass 4) and two H-nuclei (each of unit mass), accounting for its atomic weight of 14. The "protons" appear to be composed of hydrogen, and the hydrogen, in turn, to be a manifestation of electricity, but present knowledge makes exact statement very difficult.[1]

The number of *electrons* in an atom is, according to Sir J. J. Thomson, equal to its atomic number, *i.e.* the number of the atom in a series in which the atoms of all the elements are arranged approximately in the order of their atomic weights. It is now generally agreed that the protons may form a nucleus around which the electrons are aggregated in layers, not more than eight electrons occurring in stable equilibrium in any one layer, so that when more than eight electrons are present around a nucleus the surplus ones form a second layer, whilst if more than sixteen electrons are associated with one proton a third layer is formed, and so on.

According to *Moseley's Law of Atomic Structure*, the positive charge on the nucleus of an atom is N units, where N is the atomic number or sequence number of the element in the periodic table, and there are N electrons, each of unit negative charge, surrounding it to counterbalance the nucleus and form the atom.

To a very great extent the properties of protons and electrons are outside the scope of this volume and it may, for convenience, be assumed that the smallest particle

[1] A more detailed account of the structure of the atom will be found in Dr S. Miall's pamphlet, *The Structure of the Atom* (Benn Brothers Ltd.), and other special works on this subject.

which can take part in any chemical reaction is an atom—which is, consequently, the unit of all chemical calculations. A molecule—which is the corresponding unit of a compound—cannot be reduced further without decomposing the compound into its constituent atoms.

Atomic and Molecular Compounds.—Chemical compounds are divided into two classes : (*a*) atomic compounds and (*b*) molecular compounds.

Atomic compounds are formed by the interaction of atoms and are usually very stable and strongly combined. Thus, silica is produced by the combination of atoms of silicon and oxygen and is very resistant to dissociation or decomposition ; other well-known atomic compounds are alumina, the various iron oxides and other oxides, chlorides, etc.

Molecular compounds are those in which molecules (or atomic compounds) appear to combine with each other. The affinity of molecules for each other is much less than that of atoms for each other, and, consequently, molecular compounds are usually much less stable than atomic compounds. Molecular compounds are somewhat analogous to solid solutions (p. 300), and some solid solutions may be molecular compounds.

Laws of Chemical Combination.—All definite chemical compounds are formed in accordance with certain definite laws. The manner in which such compounds are produced is described in Chapter XI, but the proportions in which the various elements combine may be briefly indicated here.

Law of Fixed Proportions.—The substances which form a definite chemical compound are always united in the same proportions by weight. Thus, silica always consists of 28·3 parts by weight of silicon and 32 parts by weight of oxygen, whilst alumina always consists of 54·2 parts by weight of aluminium and 48 parts by weight of oxygen. Care should be taken to avoid confusing the names of some minerals with those of definite chemical compounds, because several minerals are known by the same name, yet do not consist of exactly the same elements in the same proportions. Thus, the term " felspar " is applied to a group of substances of similar, but not identical, composition, so that a felspar may consist of alumina, silica, and either one or more of the following metallic oxides : sodium, potassium, magnesium, and calcium. Such substances are termed *isomorphous*, as their crystals have approximately the same form, but their composition differs. For further information on *isomorphism*, see p. 334.

Other substances, on the contrary, yield identical results on analysis, and appear to possess precisely the same composition in the sense that they are composed of the same elements in the same proportions ; yet, when judged by their properties, they are wholly different substances. Such compounds are termed *isomeric*.

In all definite chemical compounds the proportion of each element is fixed and unchangeable.

Law of Multiple Proportions.—Although the composition of each definite chemical compound is fixed, or constant, some elements may combine with each other in various proportions, which are usually simple multiples of a common factor. Thus, there are several forms of iron oxide :—

Ferrous oxide contains 1 atom of iron to 1 atom of oxygen.
Magnetic oxide contains 3 atoms of iron to 4 atoms of oxygen.
Ferric oxide contains 2 atoms of iron to 3 atoms of oxygen.

Compounds containing fractional ratios of oxygen are unknown, and the same is true of all other compounds formed of elements which combine in various proportions. In other words, fractions of atoms are not considered in dealing with chemical changes ; such fractions are assumed not to exist (but see pp. 305 and 314).

Law of Equivalent Proportions.—The proportion in which two elements unite with the same weight of a third element is either the proportion in which they unite with each other or it bears a simple relation thereto. Thus, 28·3 parts of silicon unite with 32 parts of oxygen to form silica, and 12 parts of carbon unite with 32 parts of oxygen to form carbon dioxide. The silicon and carbon combine with each other in the proportions of 28·3 parts of silicon and 12 parts of carbon to form silicon carbide or carborundum. This law is very important with respect to the replacement of one substance by another in chemical compounds. Thus, 122 parts of sodium silicate contain 46 parts of sodium, whilst 204 parts of potassium silicate contain 78 parts of potassium. A mixed silicate containing both sodium and potassium will contain these metals in the proportions 46 : 78, or some simple multiple of it.

From these laws it will be seen that each element may combine with any other in one or more different proportions by weight. The smallest weight of any element which will combine with a definite weight of hydrogen or its equivalent, taken as unity, is known as the **atomic weight** of that element.[1]

The atomic weights of all the other elements have been determined on this basis and are shown in Table CIV :—

TABLE CIV.—*Atomic Weights*

Name.	Symbol.	Atomic Weight.		Name.	Symbol.	Atomic Weight.	
		O=16.	H=1.			O=16.	H=1.
Aluminium .	Al	27·1	26·78	Calcium .	Ca	40·07	39·77
Antimony .	Sb	120·2	119·24	Carbon . .	C	12·00	11·9
Argon . .	A	39·88	39·56	Cerium . .	Ce	140·25	139·0
Arsenic . .	As	74·96	74·21	Chlorine. .	Cl	35·46	35·17
Barium . .	Ba	137·37	136·27	Chromium .	Cr	52·0	51·58
Bismuth .	Bi	208·0	206·34	Cobalt . .	Co	58·97	58·4
Boron . .	B	11·0	10·9	Columbium			
Bromine .	Br	79·92	79·28	(Niobium) .	Cb	93·5	92·75
Cadmium .	Cd	112·4	111·5	Copper . .	Cu	63·57	63·06
Cæsium . .	Cs	132·81	131·75	Dysprosium .	Dy	162·5	161·2

[1] As a matter of convenience and because more accurate results can be obtained thereby, it is usual to regard the atomic weight of oxygen as 16·0 ; this makes the atomic weight of hydrogen 1·008, but the difference between this and unity is so small that it is not appreciable in ordinary work.

TABLE CIV.—*Atomic Weights*—Continued

Name.	Symbol.	Atomic Weight.		Name.	Symbol.	Atomic Weight.	
		O=16.	H=1.			O=16.	H=1.
Erbium	Er	167·7	166·07	Palladium	Pd	106·7	105·85
Europium	Eu	152·0	150·8	Phosphorus	P	31·04	30·79
Fluorine	F	19·0	18·8	Platinum	Pt	195·2	193·65
Gadolinium	Gd	157·3	156·05	Potassium	K	39·10	38·79
Gallium	Ga	69·9	69·34	Praseodymium	Pr	140·6	139·48
Germanium	Ge	72·5	71·9	Radium	Ra	226·4	224·1
Glucinum				Rhodium	Rh	102·9	102·08
(Beryllium)	Gl	9·1	9·03	Rubidium	Rb	85·45	84·77
Gold	Au	197·2	195·63	Ruthenium	Ru	101·7	100·9
Helium	He	3·99	3·93	Samarium	Sa	150·4	149·2
Holmium	Ho	163·5	162·2	Scandium	Sc	44·1	43·75
Hydrogen	H	1·008	1·00	Selenium	Se	79·2	78·6
Indium	In	114·8	113·8	Silicon	Si	28·3	28·07
Iodine	I	126·92	125·91	Silver	Ag	107·88	107·02
Iridium	Ir	193·1	191·56	Sodium	Na	23·0	22·81
Iron	Fe	55·84	55·40	Strontium	Sr	87·63	86·93
Krypton	Kr	82·92	82·26	Sulphur	S	32·07	31·82
Lanthanum	La	139·0	137·9	Tantalum	Ta	181·5	179·6
Lead	Pb	207·10	205·45	Tellurium	Te	127·5	126·49
Lithium	Li	6·94	6·88	Terbium	Tb	159·2	158·0
Lutetium	Lu	174·0	172·5	Thallium	Tl	204·0	202·38
Magnesium	Mg	24·32	24·12	Thorium	Th	232·4	230·57
Manganese	Mn	54·93	54·4	Thulium	Tu	168·5	166·8
Mercury	Hg	200·6	198·41	Tin	Sn	119·0	118·05
Molybdenum	Mo	96·0	95·23	Titanium	Ti	48·1	47·7
Neodymium	Nd	144·3	142·5	Tungsten	W	184·0	182·52
Neon	Ne	20·2	20·04	Uranium	U	238·5	236·6
Nickel	Ni	58·68	58·21	Vanadium	V	51·0	50·65
Niton (Radium				Xenon	X	130·2	129·16
emanation)	Nt	222·4	220·6	Ytterbium	Yb	172·0	170·73
Nitrogen	N	14·01	13·9	Yttrium	Y	89·0	88·3
Osmium	Os	190·9	189·38	Zinc	Zn	65·37	64·85
Oxygen	O	16·00	15·87	Zirconium	Zr	90·6	89·88

Thus, the smallest amount of chlorine which will combine with hydrogen is in the proportion 35·5 parts of chlorine to 1 part of hydrogen.

The **molecular weight** of a substance is the relative weight of that substance compared with hydrogen, the molecular weight of which is assumed to be two. When the vapour density of a substance is known, the *molecular weight* will be twice the

vapour density, and as only whole atoms can be present in a definite chemical compound, the molecular weight may be found by adding together the atomic weights of the various elements composing it. When more than one atom of any one element is present, the number of such atoms must be ascertained. The molecular weight found in this way is sometimes termed the **formula-weight**, as it is calculated from the formula (p. 306). In some cases, the formula-weight may not be the true molecular weight, because the formula may have been reduced to its simplest terms, whereas the molecule may be complex and contain two or more atoms of each kind.

The term " molecular weight " is often used in connection with ceramic materials when the term " formula-weight " would be more correct. Sometimes, also, in the ceramic industries, the term " molecular weight " has not quite the same significance attached to it as is described above. Thus, in representing the composition of glazes by means of a formula, fractions of atoms are frequently shown, though, in reality, such fractions cannot exist. The sole purpose of using fractions is to keep the numbers in the formula as small and readily comparable as possible.

Valency.—The force with which two or more atoms can unite is known as " chemical affinity," but the term " valency " is used for expressing the same idea in a somewhat different manner. Hence, the valency of an element is the number of atoms of hydrogen or its equivalent which will combine with one atom of the given element. Thus, elements which combine with or replace one atom of hydrogen are univalent. Where two atoms of hydrogen will combine with one atom of the given element, the latter is divalent. Other elements are trivalent, quadrivalent, and so on. Some elements combine in several different proportions and are then termed *polyvalent.*

According to Sir J. J. Thomson, the number of electrons in the outer layer of an atom indicates the combining power or valency of the element. He has suggested that if this is the case, each element should have two valencies, namely, (i) that represented by the number of electrons in the outer layer, and (ii) this number subtracted from eight. Langmuir, however, considers that the numbers of electrons in successive layers are respectively 2, 8, 8, 18, 18, and 32.

The following list shows the highest valencies of the principal elements occurring in ceramic materials :—

Univalent.—Hydrogen, lithium, potassium, sodium.

Divalent.—Barium, beryllium, calcium, magnesium, strontium, yttrium, zinc.

Trivalent.—Aluminium, boron, cerium, lanthanum, thallium, ytterbium.

Quadrivalent.—Carbon, lead, silicon, thorium, titanium.

Quinquivalent.—Bismuth, nitrogen, phosphorus, tantalum, vanadium.

Sexivalent.—Chromium, selenium, tellurium, tungsten, zirconium, oxygen.[1]

Septevalent.—Chlorine, fluorine, manganese.

Octovalent.—Cobalt, iron, nickel, osmium, palladium, platinum, rhodium, ruthenium.

Chemical compounds are known as *saturated* or *unsaturated*, according as they have

[1] Although oxygen is stated to be sexivalent, it is normally divalent. Similarly, carbon is sometimes divalent.

their maximum valencies satisfied or not. A molecule of an unsaturated compound can combine with further atoms so as to form a saturated compound.

The valency of an element is sometimes represented by one or more lines, the number being equal to the valency. Thus, two lines represent a divalent substance, three lines a trivalent one, and so on (p. 308).

Chemical Notation.—The composition and constitution of some chemical compounds is so complex that, in order to express it and the changes which such compounds undergo, or the reactions in which they take part, in as brief and simple a manner as possible, a chemical notation has been adopted in which each element is expressed by a symbol consisting of the first letter of its Latin name, with another letter added where several elements each have the same initial letter, so as to avoid confusion.[1] The symbol or formula of a chemical compound is expressed by writing the symbols of the various constituents one after another. The number of atoms of each element in a compound is shown by writing that number as a small figure to the right and a little below the symbol, and the number of molecules taking part in a reaction is shown by writing the number to the left of the symbol and alongside it, a full-sized figure being used. Thus, H_2O indicates one molecule of a compound (steam) composed of two atoms of hydrogen and one of oxygen, whilst the formula $CaCO_3$ indicates a compound (calcium carbonate) composed of one atom of calcium, one of carbon, and three of oxygen. It is sometimes more convenient to write this formula $CaOCO_2$, which represents the same substance as a molecular compound consisting of one molecule of lime (CaO) and one of carbon dioxide (CO_2); the lime, in turn, consists of one atom of calcium and one of oxygen, whilst the carbon dioxide consists of one atom of carbon and two of oxygen. Similarly, the formula for kaolinite (the crystalline mineral in china clay) may be expressed either as an atomic compound $H_4Al_2Si_2O_9$, or as a molecular compound $Al_2O_32SiO_22H_2O$. The latter is intended to show that, so far as the formula is concerned, the compound when heated may be decomposed into any of the following groups :—

(*a*) Two substances, $Al_2O_32SiO_2$ and $2H_2O$.

(*b*) Two substances, Al_2O_3 and $2SiO_22H_2O$.

(*c*) Two substances, $Al_2O_32H_2O$ and $2SiO_2$.

(*d*) Three substances, Al_2O_3 and $2SiO_2$ and $2H_2O$.

This mode of expression is largely used with reference to ceramic materials, as it renders complicated formulæ much easier to understand. The total number of atoms is, of course, the same, no matter whether a substance is represented as an atomic or molecular compound.

Groups of atoms or ions[2] are sometimes enclosed in brackets; for instance, $(OH)_2$ means 2 oxygen and 2 hydrogen atoms occurring in the form of two (OH) or hydroxyl groups. The use of brackets is also convenient for enclosing groups of atoms which remain united throughout the course of a reaction.

The separation of formulæ into groups should, of course, be based on experimental

[1] The symbols of the various elements are shown in Table CIV on pp. 303–304.

[2] An ion is a substance which passes to one or other electrode during electrolysis; it is also one of the two parts into which a substance is separated by electrolysis.

evidence of the manner in which substances are decomposed, and as this is not always easy to ascertain, different groupings for the same substances are sometimes used by different investigators. Thus, we find that a substance such as phakelite, the atomic proportions of which are $K_2Al_2Si_2O_8$, has been represented in the following ways by different investigators :—

(*a*) $K_4SiO_4.Al_4Si_3O_{12}$ (Rammelsberg).
(*b*) $2K_2Al_2Si_3O_{10}.K_2Al_2O_4$ (Thugutt).
(*c*) $K_2OAl_2O_32SiO_2$ (Vernadsky).

In the formula (*a*) it is regarded as a mixture of two silicates ; in (*b*) it is a mixture of an alumino-silicate and an aluminate ; and in (*c*) it is regarded as a salt of an alumino-silicic acid. Similarly, orthoclase felspar has been expressed as :

(*a*) $K_2OAl_2O_3(SiO_2)_4.(SiO_2)_2$ (Tschermak).
(*b*) $2K_2Al_2Si_3O_{10}.K_2Al_2O_412SiO_2$ (Thugutt).
(*c*) $\left.\begin{matrix}K_2Si_2O_5+Al_2Si_6O_{15}\\K_2SiO_3+Al_2Si_3O_9\end{matrix}\right\}$ (Rammelsberg).
(*d*) $K_2OAl_2O_36SiO_2$ (Vernadsky).

The last-named formula, showing felspar as an alumino-silicate, is the one now generally accepted.

In order to simplify calculations, it is customary to regard the smallest number of atoms which can be contained in a molecule of any substance as a unit for that substance, although actually solid and liquid substances do not consist of single molecules, but of arrangements of large numbers of atoms in the smallest particle which can be investigated. Thus, the formula H_2O correctly represents a molecule of steam, but a molecule of water appears to be composed of many such groups and a molecule of ice of a still larger number. Similarly, whilst SiO_2 is the formula generally used to express the composition of silica, it is most probable that that substance ought to be represented by a multiple of this formula. It has been variously suggested as Si_3O_6, Si_5O_{10}, and Si_6O_{12}, but these may be too small to be truthful. The investigations by Sir W. H. Bragg of the X-ray spectra of many solid substances have shown that the smallest particles which can compose the space-lattice formula used to represent such solid compounds must contain a much larger number of atoms.

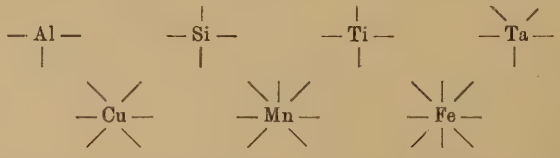
Different elements, the compounds of which have the same general properties, are sometimes expressed by a general symbol such as R ; thus, Na_2O, K_2O, and similarly constituted oxides may be represented by the formula R_2O, whilst such oxides as CaO, MgO, etc., may be represented by RO, such oxides as Fe_2O_3 and Al_2O_3 by R_2O_3, and silica, titania, tin oxide, etc., are represented by the general formula RO_2.[1] By this means a considerable simplification may often be effected without serious risk of error. This method is largely used as a means of comparing the effective composition of glazes and pottery bodies.

The value of such simplified formulæ is doubtful, as the behaviour of equal

[1] Ceramists frequently use the term RO for all fluxing oxides, irrespective of the number of atoms in them. Thus, it is used indiscriminately for one molecule of K_2O, Na_2O, CaO, or MgO respectively (see p. 310).

molecular proportions of various oxides is by no means the same, especially as regards the fusing point and the nature of the fused mass.

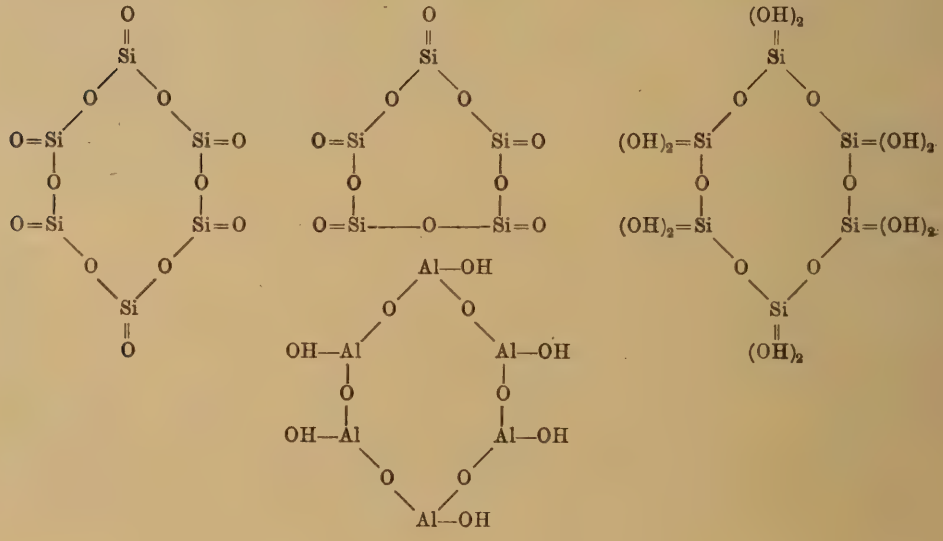
Structural or Graphic Formulæ.—In some cases, the composition of a substance may be expressed in such a manner as to include the valency (p. 305) of the various elements concerned to show more clearly than the ordinary formula how a compound can be dissociated. In the "rational" formula of a substance, each symbol has a number of lines attached to it, according to the valency or combining power of the respective element. Thus, a monovalent element is expressed by a symbol and one line (H—, K—, or Na—), a divalent element by a symbol and two lines (—Ba—, —Ca—). Others have similar lines according to their valencies.



A rational formula is built up from the symbols of the elements using the valency lines in such a manner as to show whether all the valencies of the elements are satisfied. Thus, potassium oxide is expressed as K—O—K and silica as O=Si=O. In each case, each element has the number of lines corresponding to its valency.

Rational formulæ may be arranged to show kinds of compounds, viz. : (*a*) *string* or *chain compounds*, in which the elements are strung out in a line as potash and silica (above), and (*b*) *ring compounds*, in which the elements are represented as forming a closed ring. Combinations of ring and chain compounds are also known.

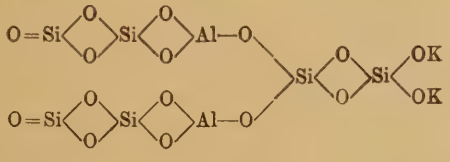
The following are examples of ring formulæ applied to ceramic materials :—



For abbreviated methods for representing ring compounds of silicon and aluminium see *The Silicates in Chemistry and Commerce*, by W. and D. Asch (Constable).

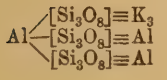
A correct structural or graphic formula is of great value in predicting new facts not yet experimentally ascertained, but care should be taken not to abuse the use of such formulæ by a merely dextrous rearrangement of the formulæ without any experimental basis. The various permutations and combinations possible with extensive formulæ lead to many possible compositions being represented, some of which are entirely fanciful and have no experimental justification. As a consequence of this and of the difficulties experienced in attempting to ascertain what is the correct formula for some substances, some investigators are not agreed as to the construction of various graphic formulæ. Thus, the constitutional formula for orthoclase felspar has been expressed in the following ways :—

(1)



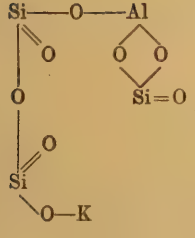
(Tschermak)

(2)



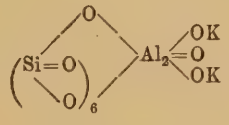
(Clarke)

(3)



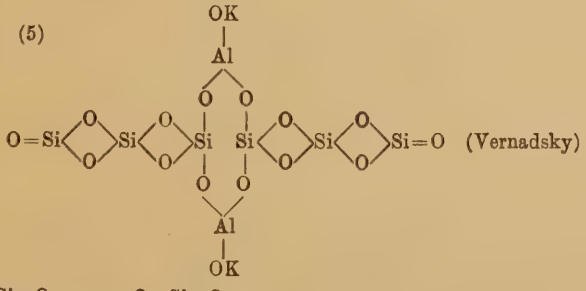
(Groth)

(4)



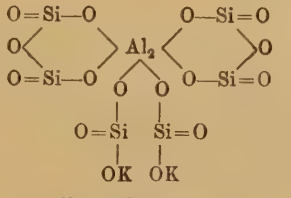
(Wartha)

(5)



(Vernadsky)

(6)



(Mellor and Holdcroft)

Similarly, the graphic formula of clay has been expressed in various ways, Mellor preferring a combined ring and chain formula, whilst W. and D. Asch use a series of closed rings (see section on *The Constitution of Clays*, p. 343).

Molecular Formulæ.—In ceramic processes many of the chemical compounds used and the reactions which take place are not fully understood, so that it is impossible to apply definite chemical formulæ. For the sake of convenience, however, and to facilitate comparison, a modified type of formula (termed a molecular formula) is

often used, not necessarily to denote a chemical compound, the molecules of which contain a definite number of atoms, but simply to show the molecular proportions of each constituent. Thus, whilst in pure chemistry $Al_2O_3SiO_2$ would represent a definite aluminium silicate (sillimanite), in the ceramic use of this formula it could equally well represent either sillimanite or a mere mixture of silica and alumina without in any sense implying any chemical combination. A molecular formula, as used in the ceramic industries, is, therefore, a grouping of the various constituents present in a special manner, to facilitate comparison, but not necessarily to denote chemical combination. The method of classification adopted is based on the amount of oxygen present, the elements (other than oxygen) being always reckoned as oxides. Any entirely volatile constituents are disregarded, calcium carbonate being taken as calcium oxide, as the carbon dioxide takes no part in the composition of the fired material. Partially volatile constituents may or may not be included according to the extent to which they persist in the final product.

In molecular formulæ the constituents are grouped as follows :—

(*a*) Metallic oxides of the R_2O and RO type (p. 307).

(*b*) Metallic oxides of the R_2O_3 type (p. 307).

(*c*) Non-metallic and sometimes metallic acid oxides of the RO_2 type (p. 307).

It is customary (following a suggestion of Seger) to take the total number of molecules in group (*a*) as unity. This involves the use of fractions of atoms, which is theoretically objectionable, but is a great practical convenience. An ideal ceramic molecular formula is represented by $RO.xR_2O_3.yRO_2$. Thus, the following is the molecular formula of a pottery body :—

$$\left.\begin{matrix}0{\cdot}81\ CaO\\0{\cdot}06\ K_2O\\0{\cdot}13\ Na_2O\end{matrix}\right\}0{\cdot}09\ Al_2O_3.4{\cdot}6SiO_2.$$

It will be seen that the basic R_2O and RO oxides are classed together at the beginning of the formula, whilst the acid, silica, is at the end. In the centre is the R_2O_3 group, which may act either as an acid or as a base according to circumstances.

It is sometimes difficult to decide in which group to place certain constituents. Thus, borax is reckoned as Na_2O and B_2O_3 and would in the ordinary way be classed with the other R_2O_3 compounds, and yet it is suggested by some investigators that the behaviour of R_2O_3 in glazes is such that it should be placed with the RO_2 group. Fluorine is generally expressed as if it were free fluorine and is placed with the silica in the RO_2 group. J. E. Hansen, however, suggests that it would be preferable to introduce the fluorine as a compound in the correct position in the formula according to whether it is basic, amphoteric, or acid. Thus, CaF_2 would be placed in the RO group, Al_2F_6 in the centre of the formula, and SiF_4 in the RO_2 group. He suggests that other compounds containing fluorine should be reduced to their simplest compounds and inserted in the proper place ; thus, cryolite should be represented partly as Al_2F_6 and partly as Na_2F_2. Sodium silico-fluoride should be represented partly as Na_2F_2 and partly as SiF_4. This would give an indication of the mineralogical constituents.

The opacifying and, therefore, feebly soluble constituents in glazes, such as TiO_2, SnO_2, SbO_2, and ZrO_2 are usually grouped separately.

It will be noticed that in a ceramic molecular formula the whole of the molecules corresponding to the chemical composition of a material are not always given. Thus, as explained on p. 310, the volatile constituents are purposely omitted.

Apart from these variations the general principles employed in building up a ceramic molecular formula are that given on p. 310.

Calculation of Percentage Composition from Molecular Formulæ.—To calculate the parts by weight or the percentage composition of a compound or mixture,[1] from the formula of the type described in the foregoing pages, the following method is used: Multiply the number of molecules of each constituent or group in the formula by the molecular weight of that constituent. Add the results so obtained together, then multiply each result by 100 and divide each in turn by the total of the results. If the arithmetical work has been correctly done the total of the results finally obtained will be exactly 100.

Example.—To find the percentage composition of pure china clay corresponding to the formula $Al_2O_32SiO_22H_2O$, multiply

1 mol. of Al_2O_3 by 102	= 102
2 mols. of SiO_2 by 60	= 120
2 mols. of H_2O by 18	= 36
	258
$102 \times 100 = 10{,}200 \div 258$	= 39·53
$120 \times 100 = 12{,}000 \div 258$	= 46·52
$36 \times 100 = 3{,}600 \div 258$	= 13·95
	100·00

The required percentage composition is, therefore, 39·53 per cent. of alumina, 46·52 per cent. of silica, and 13·95 per cent. of water.

When it is desired to produce a substance having the same composition as that corresponding to a given formula, it may be desirable to use materials which lose some of their constituents when heated. In that case, it is desirable to ascertain the molecular formula corresponding to the various materials available and to substitute a number of molecules of each material corresponding to the number of molecules in the formula.

Example.—To find the proportions of felspar ($K_2OAl_2O_36SiO_2$),[2] china clay ($Al_2O_32SiO_22H_2O$),[2] and flint (SiO_2),[2] required to produce a hard porcelain having the formula $K_2O5Al_2O_321SiO_2$.

It is obvious that all the K_2O in the porcelain formula must be derived from the felspar, so

---

[1] Strictly, a mixture cannot have a chemical formula, as its composition is not wholly homogeneous, but in order to simplify various calculations such formulæ are applied in ceramics to mixtures as well as to chemical compounds (see p. 310).

[2] Simple formulæ are assumed for convenience. The formulæ exactly corresponding to the materials available should be calculated from their analysis.

that as there is one molecule of K_2O, one molecule of felspar ($K_2OAl_2O_36SiO_2$) must be used. But this felspar also introduces one molecule of alumina and six of silica. Deduct from the formula of the porcelain that of one molecule of felspar, thus :

Porcelain formula	$K_2O\ 5Al_2O_3\ 21SiO_2$
(*a*) 1 mol. felspar	$K_2O\ \ Al_2O_3\ \ 6SiO_2$
First difference	$4Al_2O_3\ 15SiO_2$

The difference must be made up of clay and flint in a similar manner. Thus, it will be seen that the necessary alumina can be supplied by molecules of the clay which also supply some of the silica. On deducting 4 molecules of clay from the result previously obtained

First difference (above)	$4Al_2O_3\ 15SiO_2$
(*b*) 4 mol. of clay [1]	$4Al_2O_3\ \ 8SiO_2$
Second difference	$7SiO_2$

there is a surplus of 7 molecules of silica ; this would be supplied by 7 molecules of flint

Second difference (above)	$7SiO_2$
(*c*) 7 mol. of flint	$7SiO_2$
Final difference	Nil.

Adding together (*a*), (*b*), and (*c*), it will be found that the total contains the potash, alumina, and silica in the same proportions as in the original formula, but in addition are the other ingredients present in the materials used. (In this instance, the only additional material is the "water" in the clay, but in practice various "impurities" would be introduced.) The new formula, corresponding to the original one, is, therefore,

1 mol. of felspar	$K_2O\ Al_2O_3\ 6SiO_2$
4 mol. of clay	$4Al_2O_3\ 8SiO_2$
7 mol. of flint	$7SiO_2$

The percentage of felspar, clay, and flint required is then found as described on p. 311.

	Mol. Wt.	Per cent.
1 mol. felspar	$\times 556 = 556$	$\times \frac{100}{2008} = 27{\cdot}69$
4 mol. clay	$\times 258 = 1032$	„ $= 51{\cdot}40$
7 mol. flint	$\times\ 60 = 420$	„ $= 20{\cdot}91$
	2008	100·00

Calculation of Molecular Formulæ.—The formula of a compound or mixture may be calculated from the percentage composition in the following manner :—

(*a*) Find, from the percentage chemical composition of each substance used in the mixture (usually by analysis), the corresponding weight of each constituent.

(*b*) In the case of a mixture, add together all the identical constituents.

(*c*) Divide the total amount of each constituent by its molecular weight.

(*d*) Rearrange the results in the order RO, R_2O_3, RO_2.

(*e*) Divide the result by the total number of molecules of RO so as to make RO=1.

Example.—To find the molecular formula of a ball clay composed of 49 per cent. silica, 36 per cent. alumina, 1 per cent. of lime, 2 per cent. potash, and 12 per cent. of water.

(For simplicity, all constituents of less than 1 per cent. are omitted in this example, but they should be included in actual practice.)

The percentage composition required by (*a*) is given above. As this is not a mixture, section (*b*)

[1] The $8H_2O$ in 4 molecules of clay, being volatile, is excluded from the calculation.

is not required, so proceed at once to (*c*) and divide the constituents of the material by their respective molecular weights.

Silica	49 ÷ 60 = 0·817
Alumina	36 ÷ 102 = 0·353
Potash	2 ÷ 94 = 0·210
Lime	1 ÷ 56 = 0·018
Water	12 ÷ 18 = 0·670

The figures in the last column show the molecular ratios in which the various substances are present. In accordance with (*d*) these are arranged as follows :—

$$\left.\begin{matrix}0{\cdot}018\ CaO\\0{\cdot}021\ K_2O\end{matrix}\right\}\ 0{\cdot}353\ Al_2O_3\ 0{\cdot}817SiO_2\ 0{\cdot}670H_2O,$$

and in accordance with (*e*) the figures are divided by 0·040 the total of RO molecules present, the final result being :

$$\left.\begin{matrix}0{\cdot}46\ CaO\\0{\cdot}54\ K_2O\end{matrix}\right\}\ 9{\cdot}05\ Al_2O_3\ 20{\cdot}95SiO_2\ 17{\cdot}2H_2O,$$

which is the required molecular formula. It will be observed that it corresponds fairly closely, but not exactly, with the formula of kaolinite, $Al_2O_3.2SiO_2.2H_2O$, to which the purest clays bear a close resemblance.

Example.—Find the molecular formula corresponding to a glaze composed of

Cornish stone	34
Felspar	34
Whiting	22
Flint	10

(*a*) From the chemical composition, the weights of the various constituents are :—

	Potash, K_2O.	Soda, Na_2O.	Lime, CaO.	Alumina, Al_2O_3.	Silica, SiO_2.	Other Ingredients.[1]
Cornish stone . .	1·94	1·02	0·44	5·64	23·94	1·02
Felspar . . .	3·78	0·75	0·10	6·49	22·37	0·51
Whiting . .	..	..	12·32	..	..	9·68
Flint . . .	..	..	..	..	9·84	0·16
Totals . .	5·72	1·77	12·86	12·13	56·15	11·37

(*b*) The result of adding the various constituents common to two or more materials is shown in the line marked " Totals."

(*c*) Dividing each of these " totals " by its molecular weight gives :—

	Mol. Wt.
5·72 Potash	÷ 94 = 0·061
1·77 Soda	÷ 62 = 0·029
12·86 Lime	÷ 56 = 0·230
12·13 Alumina	÷ 102 = 0·119
56·15 Silica	÷ 60 = 0·936

[1] For the sake of simplicity, these are not considered in working out this example, though where the results are important they should be included.

(*d*) Rearranging the figures in the last column gives :—

$$\left.\begin{matrix}0{\cdot}061\ K_2O\\0{\cdot}029\ Na_2O\\0{\cdot}230\ CaO\end{matrix}\right\}0{\cdot}119\ Al_2O_3\quad 0{\cdot}936\ SiO_2.$$

(*e*) Dividing these figures by 0·32, the total of the RO group, gives :—

$$\left.\begin{matrix}0{\cdot}19\ K_2O\\0{\cdot}09\ Na_2O\\0{\cdot}72\ CaO\end{matrix}\right\}0{\cdot}37\ Al_2O_3\quad 2{\cdot}93\ SiO_2.$$

As noted on p. 311, it is convenient, though not strictly correct, to represent fractions of molecules ; this is done in ceramics in order to facilitate comparisons of various materials. For some purposes, *e.g.* in comparing clays, it is more convenient to take the alumina in the formulæ as unity, and it is sometimes desirable to multiply the formulæ by 100 so as to clear them of fractions.

The chief disadvantage of the use of molecular formulæ is that small proportions of some constituents may be excluded and yet may have an important influence on the material. Thus, the position of iron compounds is anomalous, for whilst ferrous oxide should be placed in the RO group, ferric oxide does not behave like alumina and cannot conveniently be placed with it. Moreover, if a material containing ferric oxide is heated in a reducing atmosphere, some ferrous oxide will be formed, though the amount is difficult to ascertain. Titanium oxide is another substance it is difficult to place properly, though it should apparently be in the RO_2 group. Colouring agents are not generally included in the formula, so that a colourless glaze may appear to have the same formula as a deep blue glaze, the amount of cobalt oxide required to give this colour being quite small.

A still more serious objection to the use of molecular formulæ is that the behaviour of a substance is not dependent entirely upon its chemical composition, and, though it may seem a comparatively minor matter, yet, as the physical characteristics—which are so important—are not considered in a formula, serious errors may arise. Thus, felspar and flint may be substituted in a glaze for Cornish stone without altering the formula, but the two glazes would behave very differently and one might be quite satisfactory whilst the other is useless. The physical properties of the constituents must, therefore, be taken into consideration as well as their chemical composition.

In the examples given on pp. 311–314 a means of simplification (namely, the omission of small percentages of constituents) is used, which may, in practice, lead to serious errors. Even more objectionable is the practice, often found in technical classes, of using typical analyses for the calculations. So far as the instructor of the students is concerned there is no objection to such typical analyses being used ; but when, as is sometimes the case, such analyses are used in investigations or in works practice instead of direct analyses of the actual materials available, serious errors may arise. A further error may be due to " rounding " off the figures in a formula in order to make them into whole numbers or to eliminate troublesome fractions.

In spite of the disadvantages mentioned, however, the use of molecular formulæ

is very convenient in facilitating comparison as well as in making complicated reactions more easy to understand.

Norms.—A method originally devised for studying the nature of rocks,[1] but applied by H. F. Staley [2] to ceramic materials, which overcomes some of the objections to molecular formulæ, consists in the use of *norms*. This mode of calculation is based on the assumed satisfaction of the bases in the order of their activity with alumina and silica and reckoning any excess as free silica or alumina. According to Cross, Iddings, Pierson, and Washington, the relative affinity of various substances for silica, beginning with the strongest, is : K_2O, Na_2O, CaO, MgO, FeO, Al_2O_3, Fe_2O_3. Similarly, the relative affinity of oxides for alumina is : K_2O, Na_2O, CaO, MgO, FeO. Ferric oxide does not combine with alumina. These investigators also claim that, in fused masses, each base first unites with as much alumina as possible and a corresponding amount of silica ; any surplus base then forms the highest silicate possible under the conditions obtaining, some or all of the following compounds being assumed to be produced :—

Low Silica.	Higher Silica.
$K_2O\ Al_2O_3\ 4SiO_2$, leucite.	$K_2O\ Al_2O_3\ 6SiO_2$, orthoclase.
$Na_2O\ Al_2O_3\ 2SiO_2$, nephelite.	$Na_2O\ Al_2O_3\ 6SiO_2$, albite.
$CaO\ Al_2O_3\ 2SiO_2$, anorthite.	..
$K_2O\ SiO_2$, potassium metasilicate.	..
$Na_2O\ SiO_2$, sodium metasilicate.	..
$2CaO\ SiO_2$, calcium orthosilicate.	$CaO\ SiO_2$, calcium metasilicate.
$2ZnO\ SiO_2$, zinc orthosilicate.	$ZnO\ SiO_2$, zinc metasilicate.
$2PbO\ SiO_2$, lead orthosilicate.	$PbO\ SiO_2$ lead metasilicate.

The following examples of classification by " norms " are due to H. F. Staley.

Molecular formula .	$\left\{\begin{matrix}0{\cdot}5\ Na_2O\\0{\cdot}5\ CaO\end{matrix}\right\}\ 1{\cdot}5\ SiO_2$	$\left\{\begin{matrix}0{\cdot}5\ Na_2O\\0{\cdot}5\ CaO\end{matrix}\right\}\ 0{\cdot}2\ Al_2O_3\ 2{\cdot}4\ SiO_2$
Norm . . .	$0{\cdot}5\ Na_2O\ \ 0{\cdot}5\ SiO_2$ $0{\cdot}5\ CaO\ \ 0{\cdot}5\ SiO_2$ $0{\cdot}5\ SiO_2$	$0{\cdot}2\ Na_2O\ \ 0{\cdot}2\ Al_2O_3\ 1{\cdot}2\ SiO_2$ $0{\cdot}3\ Na_2O\ \ 0{\cdot}3\ SiO_2$ $0{\cdot}5\ CaO\ \ 0{\cdot}5\ SiO_2$ $0{\cdot}4\ SiO_2$

The use of norms in the study of molten or partially molten materials is often convenient, though not necessarily exact ; it often suggests what might occur under favourable conditions, and very often the substances predicted by a " norm " calculation are very similar to those actually found ; in many cases, however, the results are quite hypothetical.

Triaxial Diagrams.—When a large number of similar substances are to be compared, as in ascertaining the effect of certain constituents on a glaze or pottery body, a particularly useful means of simplifying the work is to employ a Stokes' triaxial diagram (see Chapter XI).

[1] *Quantitive Classification of Igneous Rocks* (Cross, Iddings, Pierson, and Washington).
[2] *Trans. Amer. Cer. Soc.*, **13**, 130 (1911).

Chemical Equations.—The initial and final products of a chemical reaction may be expressed briefly and clearly by arranging their formulæ in the form of an equation, the reacting substances being placed on the left-hand side of the sign of equality and the resultant products on the right-hand side of it. The total number of atoms on each side of an equation must be equal. Thus, the reaction between silica and carbon in the manufacture of carborundum may be expressed as

$2SiO_2$	+	$4C$	=	$2SiC$	+	$2CO_2$
Silica.		Carbon.		Carborundum.		Carbon dioxide gas.

A single chemical equation shows only the beginning and end of a reaction and gives no indication of any intermediate ones which may occur.

Sometimes a chemical reaction is reversible if the conditions of temperature or pressure are changed; this reversibility may be indicated by substituting the sign $\rightleftharpoons$ for the usual sign of equality, the half arrows indicating that the reaction may proceed in either direction. Thus, the equation

$CaCO_3$	$\rightleftharpoons$	CaO	+	CO_2
Calcium carbonate.		Lime.		Carbon dioxide.

indicates that under favourable conditions of heat and pressure (i) calcium carbonate may be decomposed into lime and carbon dioxide; (ii) lime and carbon dioxide can combine to form calcium carbonate; and (iii) if the conditions are first favourable to reaction (i) this will occur, but if in the course of time the conditions are altered (for instance, if the pressure is increased because the carbon dioxide gas cannot escape) reaction (ii) may commence and all further progress with reaction (i) will cease. The importance of these reversed reactions is often overlooked (see also Chapter XI).

Acids, Bases, and Salts.—Many chemical compounds are classed, according to the manner in which they react with each other, as *acids*, *bases*, and *salts*, the last-named term being frequently extended to include all compounds which are neither acids nor bases.

An *acid* cannot be defined satisfactorily, because there is no single criterion of acidity. When the matter is carefully investigated, all the usual definitions of acids are found to be faulty. Thus, the old definition that an acid is a substance which combines with a base to form a salt is very unsatisfactory, because it attempts to define an acid in two unknown terms—base and salt, and, whilst such a definition is often useful, it is far from being ideal. On the other hand, the usual modern definition of an acid as a substance which liberates free hydrogen ions when it is dissolved in an ionising solvent, excludes all insoluble acids and some soluble ones, including silicic acid. Similarly, the definition that an acid is a hydrogen salt is often convenient, but in the absence of a reliable definition of a salt it is unsatisfactory. The subject is further complicated by the fact that silica and some other substances act, at high temperatures, in a manner precisely similar to acids at lower temperatures, except that they do not contain hydrogen. Thus, silicic acid, H_2SiO_3, is soluble in water and reacts with caustic soda to form a soluble sodium silicate and free water. Silica

(SiO_2) is insoluble in water and has only one obviously acid character, viz. it combines with caustic soda in the same manner as silicic acid, except that only half the water is liberated, thus :

(i) $2NaOH+H_2SiO_3=Na_2SiO_3+2H_2O$;
(ii) $2NaOH+SiO_2 \quad =Na_2SiO_3+H_2O$.

In such cases, silica behaves as an *anhydride* (*i.e.* an acid which has parted with one or more molecules of water), but it is commonly referred to as an acid, though this is not strictly correct.

On the other hand, silicic acid, H_2SiO_3, is not ionised when dissolved in water and so cannot be included among the acids, which are defined in terms of their ionisation products. Silicic acid can only be regarded as an acid in this sense by a process of analogy, inasmuch as its sodium salt Na_2SiO_3 is soluble in water and on electrolysis is readily ionised.

Many acids may be regarded as consisting of two parts : (i) the hydrogen which can be liberated on ionisation, and (ii) the remaining portion which is frequently termed the *acid radicle*.[1] This term is misleading, as soluble acids owe their acid properties to the free H-ions and are inert when the conditions are such that no free H-ions exist. If, however, the term " acid radicle " is regarded as that part of an acid which enters into the resultant salt and it is also understood that it is not, in itself, able to confer acid properties, it may be used with great convenience and without much risk of serious error. In a molecule of a soluble acid, the " acid radicle " and the negative ion are identical, but, in insoluble acids, the existence of ions cannot be proved and the term " radicle " may then be preferable.

Both a radicle and an ion may consist of several atoms, and these may retain their grouping when the substance of which they form a part undergoes certain chemical changes, such as the reaction of an acid and a base to form a salt. Thus, sulphuric acid consists of two radicles—the hydrogen ion (H_2) and the negative ion (SO_4). The term " acid radicle " is also largely used for a purely imaginary grouping of atoms, such as SO_3, SiO_2, etc., these groups being really the anhydrides of the corresponding acids. Such a grouping is convenient when salts are regarded as molecular rather than ionic compounds. Thus, sulphuric acid may be regarded in three ways as composed of

(i) H_2 ions and SO_4 ions.
(ii) H ions and HSO_4 ions.
(iii) H_2O ions and SO_3 ions (radicles).

Both of the first two conceptions agree with the facts. The third conception does not agree with the facts respecting soluble acids, but it is a convenient method of expressing reactions between bases and anhydrides and other apparently acid substances which are devoid of hydrogen.

The names of acids give some idea of their composition and properties. Thus, acids

[1] A radicle is a group of atoms which can enter or leave a molecule without the elements in it being separated. Typical radicles are K_2O, Al_2O_3, SiO_2, SO_3, etc.

may have the suffixes *ic* or *ous*, according to the ratio of oxygen atoms to hydrogen atoms in them. Thus, sulphur*ic* acid (H_2SO_4) has more oxygen in its molecule than sulphur*ous* acid (H_2SO_3), nitr*ic* acid (HNO_3) has more than nitr*ous* acid (HNO_2). Where several similar compounds are known, for those which contain less oxygen than in the ones designated by the suffix *ous*, the prefix *hypo* is used, *e.g.* hyposulphurous acid, whilst for compounds which contain more oxygen than in those designated by the suffix *ic*, the prefix *per* is used, *e.g.* perchloric acid.

Whilst the term "acid" is usually defined so as to be applicable only to those compounds from which hydrogen can be liberated when they are ionised, the term is frequently applied to elements or groups of elements which, in combination with hydrogen or water, will produce an acid. Thus, silica, SiO_2, is frequently regarded as an acid because, in combination with water, it produces a true (silicic) acid ($H_2O+SiO_2=H_2SiO_3$). Similarly, carbon dioxide is often regarded as an acid, because when dissolved in water it forms carbonic acid ($H_2O+CO_2=H_2CO_3$). Alumina sometimes acts as an acid ($H_2O+Al_2O_3=H_2Al_2O_4$), and sometimes as a base (as in the alums). These uses of the term "acid" are based on the erroneous idea that the SiO_2, CO_2, or other corresponding radicle conferred the acid properties, and such radicles were, in consequence, frequently termed "acid-radicles." It is now known that the acidic property of a substance can only be produced if it contains hydrogen in a certain form. Nevertheless, it is often convenient—provided its limitations are understood—to regard the portion of an acid combined with the hydrogen as an acid-radicle, and the assumption that any substance which combines with a base to form a salt may be regarded as an acid is largely used in the ceramic industries.

The study of a book on elementary inorganic chemistry sometimes leads to the conclusion that acids are of a comparatively simple composition, whereas some of the acids in ceramic materials are very complex. Thus, whilst silicic and aluminic acids are fairly simple, such acids as various alumino-silicic acids, in which the acid radicle contains the elements of silicon, alumina, and oxygen are often extremely complex. One of the simplest alumino-silicic acids may be represented by $H_4Al_2Si_2O_9$, or $2H_2OAl_2O_32SiO_2$, the respective ions being H_4 and $Al_2Si_2O_9$, but in the ceramic usage of the term "acid" (*supra*), the oxygen connected with the hydrogen ions is omitted from the acid radicle and $Al_2Si_2O_7$ or $Al_2O_32SiO_2$ is regarded as the acid radicle of alumino-silicic acid. A still further abbreviation (though an inaccurate one) is obtained as described above, by regarding the acid radicle as though it were itself an acid.

In this sense, the chief acid materials used in the ceramic industries are silica and clay, the former representing silicic acid the latter a group of alumino-silicic acids. Alumina—which sometimes behaves like silica—is not commonly regarded as an acid, though in some compounds it behaves as an acid radicle and forms aluminates.

The characteristic properties of most acids are (i) their sour taste; (ii) their power of corrosion; and (iii) their power of uniting with bases to form salts. All these properties are usually evident at ordinary temperatures. The acid substances used in the ceramic industries do not possess these properties at ordinary temperatures,

and the second and third only become evident at temperatures exceeding about 700° C.; at ordinary temperatures, such acids appear to be inert solids. Thus, whilst clay is of an acid character and lime is basic, they do not react on each other at ordinary temperatures, but must be heated to a temperature of 700° C. or more before any reaction occurs. Consequently, the truly "acid" nature of the alumino-silicic acids has been largely overlooked—often with serious results.

A *base* is equally as difficult to define as an acid. The usual definition of a base as a compound of a metal (or a group of elements equivalent to a metal), capable of replacing the hydrogen ions in an acid when the two are placed in contact under suitable conditions, is open to the objection that it is impossible to define an acid satisfactorily. A base may also be defined as a compound which can be resolved into two ions, one of which is the hydroxyl (OH) ion; but this definition is unduly restrictive, as many substances which act as bases do not contain the OH-group, though most of them are readily converted into hydroxides when in contact with water.

A third definition of a base is that it is a substance which will react with an acid to form a salt. This is the definition most widely used in the ceramic industries, not because it is the most accurate, but because it groups in the most convenient form a number of substances, all of which behave towards silica and other "acid" substances in a similar manner. When so broad a definition is used, the composition of a base becomes a matter of secondary importance; consequently, the term "base" is often applied to carbonates and other compounds to which the other definitions are inapplicable.

These various definitions of the term "base" are liable to be misleading unless sufficient care is taken when the term is used. Most bases are the oxides or hydroxides of a metal, or compounds of these with a weak acid (such as the carbonates), an oxide being a compound of a metal with oxygen alone, and a hydroxide or hydrate being a compound of a metal or its equivalent with oxygen and hydrogen, the two latter being united to form a *hydroxyl* group (OH), which may retain its identity when it is transferred from one substance to another by chemical reaction.

The constitution of a base is often peculiar; under suitable conditions all oxides and hydroxides can be split up into a metal and an oxygen or hydroxide ion, but many oxides, when acting as bases, combine *in toto* with acid radicles. This dual means of expressing the behaviour of bases is liable to confusion, though, when rightly understood, it is often convenient. For example, when the base sodium hydroxide (NaOH) reacts with hydrochloric acid (HCl) to form common salt, the reaction may be represented by

$$\underset{\text{Base.}}{NaOH} + \underset{\text{Acid.}}{HCl} = \underset{\text{Salt.}}{NaCl} + \underset{\text{Water.}}{HOH}$$

In this case, it is clear that the H-ion of the acid combines with the OH-group in the base, forming water, and enabling the remaining materials to form the salt. It is equally correct to represent the reaction of sodium hydrate and silicic acid in the same manner.

$$\underset{\text{Base.}}{2NaOH} + \underset{\text{Acid.}}{H_2SiO_3} = \underset{\text{Salt.}}{Na_2SiO_2} + \underset{\text{Water.}}{2HOH}$$

If the grouping of the atoms is rearranged in molecular formulæ the equation becomes

$$\underset{\text{Base.}}{Na_2OH_2O} + \underset{\text{Acid.}}{SiO_2H_2O} = \underset{\text{Salt.}}{Na_2OSiO_2} + \underset{\text{Water.}}{2H_2O}$$

If the reaction takes place at a high temperature, both the base and acid will undergo partial decomposition prior to the reaction and will lose water. The equation representing what occurs at a high temperature is then

$$\underset{\text{Basic radicle.}}{Na_2O} + \underset{\text{Acid radicle.}}{SiO_2} = \underset{\text{Salt.}}{Na_2OSiO_2}$$

This method of representation is often so convenient that its inaccuracies are commonly regarded as negligible, and various oxides, and even some carbonates, are regarded as bases simply because of their behaviour with acid radicles at a high temperature. No serious error need arise if the purpose and limitations of this mode of expression are borne in mind and if improper deductions are not drawn from it.

An *alkali* is a base of specially active character, *e.g.* sodium and potassium oxides and hydroxides. The chief bases used in the ceramic industries are bauxite and other forms of alumina, lime, magnesia, calcined dolomite, and zirconia. On account of the ease with which they are converted by heat into bases, various carbonates, such as sodium carbonate, potassium carbonate, calcium carbonate (whiting, limestone, marble), magnesium carbonate (magnesite), calcium-magnesium carbonate (dolomite, magnesian limestone), etc., are commonly referred to as " bases," though they are actual by the salts of the corresponding bases.

Oxides have special terminations according to the proportion of oxygen they contain, those ending in *ic* having more oxygen than those ending in *ous*. Sesquioxides have a proportion of oxygen intermediate between oxides whose names end in *ic* and those ending in *ous* ; sesquioxides often exert both acid and basic functions, according to the conditions to which they are exposed. Thus, alumina may act as an acid and form aluminates, or it may act as a base and form aluminium salts. Ferric oxide, Fe_2O_3, is sometimes regarded as a sesquioxide because it behaves in a similar manner.

A *salt* is commonly defined as the product of the interaction of an acid and a base, during which reaction the hydrogen of the acid is replaced by a corresponding part of the base. Such a definition is open to the objection that neither an acid nor a base can be defined satisfactorily, and therefore any definition of a salt based on these terms must be unsatisfactory. Nor does this definition include the product formed by the reactions of an anhydride or a so-called " acid oxide " such as silica with a base. In both these cases the same salts are formed as when the corresponding acids are used, so that any complete definition of a salt should include the product of a base with either an acid-oxide, an anhydride, or an acid.

A *normal salt* is one in which the valencies of both the acid and base are mutually satisfied. When only part of the replaceable hydrogen is removed, the resulting salt is termed an *acid salt*, as it possesses some acid properties, whilst, if there is an excess of base over that required to replace the hydrogen, the salt is termed a *basic salt*. A

neutral salt is one which does not combine with a further quantity of either the acidic or basic radicles, of which it is composed. The use of the term " neutral salt " to indicate that it does not affect the colour of an indicator such as litmus is meaningless unless the name of the indicator is stated, because some salts which are neutral to litmus and to methyl orange are strongly acid to phenolphthalein.

The names given to salts bear a relation to the constituents from which they have been formed. Under normal conditions the name of a simple salt will combine that of the metal and the acid radicle composing the salt, as sodium silicate, which is a self-explanatory title. The salts produced by the interaction of bases with complex acids form correspondingly complex salts. Thus, alumino-silicic acid forms alumino-silicates, silico-tungstic acid forms silico-tungstates, and so on. In the absence of oxygen the termination *ide* is generally employed, as in chlorides, carbides, silicides, etc. When oxygen is present the names of the salts terminate according to the acid from which they are derived ; thus, acids containing oxygen and whose names end in *ic* form salts whose names end in *ate*, sulphur*ic* acid forming sulph*ates*. Other examples are :

*Per*chlor*ic* acid forms *per*chlor*ates*.
Nitr*ic* acid forms nitr*ates*.
Nitr*ous* acid forms nitr*ites*.
*Hypo*chlor*ous* acid forms *hypo*chlor*ites*.

The name of the base used in forming a salt may be utilised to indicate some of the characteristics of the salt. A salt formed from a base whose name ends in *ic* may have the basic portion of its name ending in *ic*, whilst if the name of the base ended in *ous* the salt may have the basic part of its name ending in *ous*. Thus—

Base.	Salt.
Ferr*ic* oxide yields	ferr*ic* silicate. ferr*ic* sulphate. ferr*ic* chloride.
Ferr*ous* oxide yields	ferr*ous* silicate. ferr*ous* sulphate. ferr*ous* chloride.

It is sometimes convenient if the name of a substance (either a salt or other compound) indicates the number of atoms of any element in a molecule of a compound ; in that case, the number is sometimes prefixed to the name of the element, as in trimanganic tetroxide, in which there are three atoms of manganese to each four of oxygen, and in tricalcium silicate, which contains three atoms of calcium to each atom of silicon. Again, chromium sesquioxide has two atoms of chromium to each three of oxygen, whilst chromium trioxide has one of chromium to three of oxygen. The effect of acid and basic substances upon each other is further dealt with in Chapter XI.

Neutral Substances.—Substances which react with neither bases nor acids are termed *neutral*. Normal salts—which are the products of the reaction of acids and bases—belong to this class, as also do various oxides, though the latter sometimes

act as bases or as acids according to the nature of the substances with which they are brought into contact. Alumina and ferric oxide are typical examples, as they may (i) remain inert; (ii) act as bases forming aluminium or ferric salts, such as sulphates; or (iii) take the part of an acid radicle and form aluminates or ferrates with soda, potash, or lime as the base.

The activity of many substances used in ceramics depends largely on their temperature; they may be inert or neutral when cold, but actively basic or acid when at a red heat. Carbon, in various forms, chromic oxide, and even silica and clay may be included among such substances. In considering whether a ceramic material is basic, acid, or neutral, it is not sufficient to investigate its behaviour at low temperatures, because, as previously explained, many such substances do not commence to react below a dull-red heat. Failure to realise this has led to much misconception as to the nature of clays and other ceramic materials.

The investigation of these substances is still further complicated by the fact that their constitution is so complex that they do not behave in a normal manner, but break down into a corresponding number of simpler substances. For instance, a complex alumino-silicic acid such as pure china clay when fused with sodium carbonate appears to be decomposed into its constituent oxides, which combine separately with the base, water and carbon dioxide being expelled in the gaseous form. This may be represented by the equation

$$Al_2O_32SiO_22H_2O+3Na_2CO_3=Na_2OAl_2O_3+2Na_2O2SiO_2+2H_2O+3CO_2,$$

or as

$$H_4Al_2Si_2O_9+3Na_2CO_3=Na_2Al_2O_4+2Na_2SiO_3+2H_2O+3CO_2.$$

Under some natural conditions the alumino-silicates appear to retain their complex structure, as in orthoclase ($K_2OAl_2O_36SiO_2$), etc.

Molecular Structure of Solids.—Although all compound gases are composed of molecules, the ordinary conception of a molecular structure of solid substances and of some liquids does not fit some of the known properties of matter in these states. Even when solid or liquid particles are so minute as to be in the colloidal (sol) state, the ordinary conception that they have a molecular structure is scarcely applicable. Investigations of the molecular or atomic structure of amorphous substances is particularly difficult, but recent investigations of the structure of crystals has shed some light on the constitution of certain ceramic materials, and particularly on that of clay. Thus, if X-rays are passed through a crystal or through a small quantity of powdered crystals and allowed to fall upon a photographic plate, a line will be produced on the film corresponding to each important plane of atoms in the specimen used. As each substance has a definite X-ray spectrum consisting of a series of lines at definite distances apart, a mixture of two or more substances will produce an X-ray spectrum having lines characteristic of each constituent, and if the spectrum of an unknown crystalline substance is compared with those of various other substances its composition can be determined.

Bragg [1] has examined photographically the interference figures produced by the

[1] *X-rays and Crystal Structure*, G. Bell & Sons, London (1916).

reflection of X-rays by the atoms of the various elements in a crystal. By this method it is possible to calculate (*a*) how the atoms are arranged, and (*b*) the distance between the centres of the atoms.

The distance between the centres of two neighbouring atoms may be expressed as the sum of two constants represented by the radii of the corresponding spheres. The diameter of a sphere representing an atom is termed the diameter of the atom, and is usually expressed in Ångstrom units (Å$=10^{-8}$cm.).

According to modern ideas of the structure of crystalline chemical compounds, the mass is regarded as being partitioned off with space units or *space-lattices*. Analogous portions of matter are supposed to be distributed in each space unit. Each space-lattice is thus considered as being made up of units or points which represent the centres of gravity of the constituent molecules. From this point of view a crystal is an aggregate of ellipsoids or spheres so piled on one another that the corresponding axes are in accord with a definite geometrical plan. Each atom then occupies a space equal to one space unit, and the molecule may be regarded as the mass formed by the atoms arranged in a network or space-lattice. Sometimes the space-lattice may include a large number of atoms—far larger than those which form a single molecule of the substance when in a gaseous form.

Considering the elementary atoms composing crystals as points, all crystals may be described as a homogeneous arrangement of points. There are 230 modes of arranging points in a homogeneous structure such as is possible to crystals, and fundamental to these 230 modes are 14 space-lattices, defined by Frankenheim and Bravais. Hence the structure of a crystal is fundamentally that of a space-lattice or three-dimensional trellis-work, in which the particles are situated at the corners of each section or mesh of the net, so that the strings represent the lines of intersection of the planes and the knots their points of intersection.

Three of the fourteen space-lattices are of cubic symmetry, the points being arranged as a simple cube, a centred cube, and a face-centred cube respectively. Two others are tetragonal, four are rhombic, two monoclinic, one triclinic, one hexagonal, and another is rhombohedral-trigonal.

In the simplest crystals the space-lattice is directly formed by the chemical atoms, but in more complex crystals the space-lattice points may be surrounded or replaced by groups of atoms.

The crystal faces are parallel to the various planes of atoms of the space-lattice, and any three adjacent points of the lattice will determine the position of a crystal face. If all the points of a space-lattice are joined by straight lines the resulting parallelopipeda will correspond to the "bricks" of which Haüy considered crystals to be built.

In the *simple cube-lattice* the atoms are at the corners of a cube. In the *body-centred cube-lattice* the atoms are at each corner, and one other is at the centre, making nine in all. In the *face-centred cube-lattice* there is an atom at each corner and one at the centre of each face, making fourteen in all. In more complex groups a correspondingly larger number of atoms may be involved.

Most of the atoms in metals are arranged in the form of face-centred cubic space-

lattices, though some have their atoms in the form of cubes with an atom at each corner and one in the centre of each cube. A third type consists of closely packed right-triangular prisms, the bases of which are equilateral triangles and the altitudes 1·633 times the side of the triangles. The atoms in this structure are arranged at each of the prism corners and at half of the prism centres.

The simple cubic arrangement of atoms is also found in single salts having equal numbers of positive and negative atoms. Sodium chloride has a cubical space-lattice structure with atomic centres $2{\cdot}81 \times 10^{-8}$ cm. apart. Carborundum has a face-centred cubic-lattice, the atoms forming cubes with an extra atom in the centre of each face, the distance between the atomic planes being $2{\cdot}179 \times 10^{-8}$ cms. Crystals of fluorspar, magnetite, and zinc-blende are of the double face-centred space-lattice type.

W. L. Bragg found that the space-lattice structure of pyrites was rather complex, the structure being fundamentally of the face-centred cube type, but the sulphur atoms were not placed exactly equidistant from the iron atoms. He found hauerite (MnS_2), ullmanite (NiSbS), cobaltite (COAsS), and cuprite (Cu_2O) to have somewhat similar structures. W. H. and W. L. Bragg found that calcite has carbon and oxygen atoms on triangular planes perpendicular to the crystal axis. The calcium atoms lie in planes just above and just below the carbon and oxygen planes. Rhodochrosite ($MnCO_3$), siderite ($FeCO_3$), sodium nitrate ($NaNO_3$), dolomite ($MgCO_3CaCO_3$), and hæmatite (Fe_2O_3) have somewhat similar structures. Zircon, according to L. Vegard, is of the face-centred tetragonal type, as also are rutile and cassiterite.

P. Landrieu [1] states that the points of the space-lattice of double compounds may be considered as occupied by the ions of the molecules which are uniformly distributed through the lattice, giving electrostatic equilibrium. If this is the case it would account for the abundance of inorganic double compounds and their rarity amongst organic compounds. In mixed crystals, however, the points of the lattice are occupied by molecules or ions which are isoteric in the sense used by Langmuir. Thus, mixed crystals appear to be due to the replacement of ions or molecules with others with which they are isoteric.

The X-ray spectra of various substances seem to show that in a crystal there is no definite molecular structure, but that crystals consist of atoms arranged in regular order, the unit of which is what is known as a *space-lattice*, the atoms in which, though closely packed, are unconnected. In the various space-lattices which appear to be the units of crystal structure, the atoms at the surface act as though they unsaturated, and have a zone of definite chemical attraction of a thickness of at least 10^{-8} cms. This zone of attraction appears to cause the growth of crystals in a saturated solution by the attraction of atoms in the solution to the surface of the crystal. These atoms when in position attract others, the process continuing and the crystal growing until the solution will not allow any further withdrawal of atoms.

If this conception of the structure of solids is correct, it may account for the phenomena of adsorption or the attraction of atoms by solid surfaces; the forces holding adsorbed molecules are the same as those holding together the atoms of crystals, the adsorption depending on the residual valency of the adsorbed molecules.

[1] *Bull. Soc. Chim.*, **31**, 1217–41 (1921).

From the foregoing it appears that the atoms in crystals are not combined to form molecules, which in turn are aggregated to form crystals, but that a large number of atoms is aggregated in definite order to form one large structure, or "giant molecule," arranged to form a "space-lattice," and that each separate space-lattice forms a unit from which large crystals can grow by the mutual attraction of the individual atoms.

The examination of materials by their X-ray spectra has one great drawback. Numerous researches have proved that the quality and quantity of the characteristic X-rays emitted are independent of the state of the chemical combination and valency of the elements concerned. Thus, the rays emitted by $FeSO_4$, Fe_2O_3, Fe_3O_4, $(NH_4)_4FeC_6N_6$, give identical adsorption coefficients ;[1] the amount of X-rays emitted by a given weight of tin is unchanged when the tin is converted into oxide,[2] and finally the characteristic rays of Br and I are emitted by C_2H_5Br and CH_3I respectively. Hence the scattering of X-rays appears to be a purely atomic effect, and whilst they lead to a knowledge of the mean positions of the atoms they cannot, from the nature of the case, throw any direct light on the question of the existence or non-existence of molecules in the crystalline state.

Polymorphism is a modification of crystal structure (p. 5), and may be due to different causes in different substances. The chief explanations of its origin are as follows :—

1. It may be the result of a molecular change as suggested by Smits.[3]

2. It may be the result of a structural change in the arrangement of the individual components of the crystal lattices, these components being molecules, atom groups, or atoms, as suggested by Bravais. In some cases, according to Bridgeman,[4] the geometrical centres may remain constant, but the orientation of the points may vary.

3. It may be due to a change in the form of some of the atoms without there being any change in the arrangement or orientation. R. B. Sosman[5] suggests that a change may take place in the atomic nucleus or in the planetary electrons. Thus, he considers the inversion of pure iron at 770° C. to be an atomic inversion, whilst he attributes the allotropic transformation of silica partly to structural and partly to atomic changes (see also p. 328).

THE CHEMICAL CONSTITUTION OF SILICATES AND ALUMINO-SILICATES

A large number of ceramic materials are of an acid character and contain silica as an important constituent ; some of them also contain alumina. These two types of substances are respectively known as silicates and alumino-silicates.

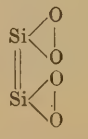
The silicates form simple salts consisting of a number of atoms of the basic radicle

[1] J. L. Glasson, *Proc. Camb. Phil. Soc.*, **15**, 437 (1910).
[2] Chapman and Guest, *ibid.*, **16**, 136 (1911).
[3] *Die Theorie der Allotropie*, Leipzig (1921).
[4] *Proc. Am. Acad.*, **52**, 91–187 (1916).
[5] *J. Wash. Acad. Sci.*, **7**, 62–67 (1917).

and a number of groups of one of the silicic acid radicles, or (what amounts to the same thing and is probably stated more correctly) they consist of positive (metallic) ions combined with negative silicic ions.

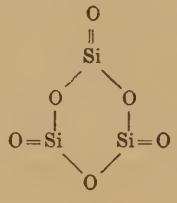
The Constitution of Silica

The silicic acid derivable from these salts is a compound of hydrogen, oxygen, and silicon, but, in many instances, in the reactions which occur with ceramic materials the anhydride replaces the acid. This anhydride is silicon oxide—well known as silica—which is usually expressed by the formula SiO_2; it is highly probable, however, that its molecule is much more complex than this formula suggests, though the silicon and oxygen atoms are in the ratio of 1 : 2. Thus, the depression of the freezing-point of lithium metasilicate caused by the addition of ignited amorphous silica was found by Schwarz and Sturm [1] to indicate the molecular formula of such silica to be Si_2O_4. This agrees with the independent investigations of J. Beckenkamp,[2] who considers silica to have the formula

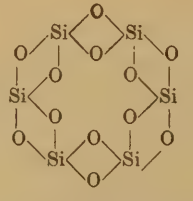


in which two oxygen atoms are more strongly linked to one silicon atom than the two silicon atoms are linked to each other.

Curie [3] gives the formula of silica as Si_3O_6 or



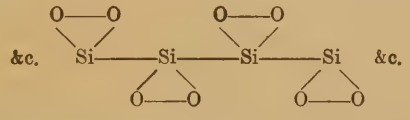
but G. Martin,[4] after examining the oxidation products of different organic silicon compounds, considers that a molecule of silica should be represented by the formula Si_6O_{12}, the atoms being arranged in the form of a hexagonal ring compound, which may be represented by the formula



[1] *Ber.*, **47**, 1735 (1914).
[2] *Z. anorg. Chem.*, **110**, 290–310 (1920).
[3] *Encyl. Chim.*, **2**, 152 (1884).
[4] *Chem. News*, 61 (1915).

W. and D. Asch [1] have made an elaborate survey of the literature on the silicates, and have concluded that silica at ordinary temperatures is a ring compound, each ring containing either five or six atoms of silicon, according to its origin. These rings they term respectively *pentites* and *hexites*. The graphic formulæ are shown on p. 308.

W. H. and W. L. Bragg consider that α-quartz consists of three inter-penetrating hexagonal space-lattices, derived from each other by equal translations parallel to the axis *c*, together with rotations of 120 degrees about that axis; Beckenkamp [2] considers that the silicon atoms in silica more probably form a rhombohedral lattice, whilst R. B. Sosman [3] considers that the silica molecule has a chain structure consisting of definite SiO_2 triplets [4] (*i.e.* groups consisting of one atom of silicon and two of oxygen), which persist in the liquid, glassy, and crystalline states, and that the allotropic forms are built up by three different combinations of the silica chains. He also considers that the triplets retain their individuality in silicates and in more complex compounds, and that the oxygen and silicon atoms in the quartz crystal occur on a helix, there being three silicon atoms to each turn of the helix and six oxygen atoms attached to them, thus forming three silica triplets. The position of the oxygen atoms will determine whether the crystal is right handed or left handed. This structure would place the oxygen atoms upon the edges of an imaginary hexagonal prism containing silicon atoms of corresponding planes. He considers each silica triplet to be constructed as follows: there are three atoms, the two oxygen atoms each consisting of two electrons surrounded by six others. The silicon atom consists of two electrons surrounded by twelve others. The silicon atom shares one pair of electrons with each oxygen atom, and the oxygens share a pair of electrons between them. The silica also shares a pair of electrons with each of two neighbouring silicon atoms, thus forming a thread or chain structure having the form



the silica triplets forming threads or wires which are in rapid motion whilst the silica is in the liquid or fused state, but which, on cooling, form an intimately tangled mass which, if drawn out, as in glass tubes, would cause the wires to be parallel to the rod or tube. This would explain the difference in the expansion in a direction parallel to and that in one perpendicular to the axis of the rods, as observed by Callendar.[5] Rayleigh [6] also noticed the ribbon-like crystallisation of silica glass rods.

Silica occurs in various allotropic forms which are stable at different temperatures. These are shown in Table CV.

[1] *The Silicates in Chemistry and Commerce* (Constable & Co., Ltd., London).

[2] *Loc. cit.*, p. 326.

[3] *J. Franklin Inst.*, **194**, 741–64 (1922).

[4] The term "*triplet*" is used by him instead of "molecule," as the latter term has other connotations which are not applicable in this instance.

[5] *Phil. Mag.*, **23**, 998–1000 (1912).

[6] *Proc. Roy. Soc., London*, A **98**, 284–96 (1920).

TABLE CV.—*Forms of Silica*

Amorphous. .	Amorphous silica	Precipitated silica. Silica glass.
Crystalline . .	Quartz . .	α-quartz. β-quartz.
	Tridymite .	α-tridymite. β-tridymite.
	Cristobalite .	α-cristobalite. β-cristobalite.

The nature and stability ranges of these various forms of silica have been very fully investigated during recent years, but they are not yet fully understood. This is partly due to the low thermal conductivity of silica and silicates generally, which renders the rate of any changes which may occur very slow.

R. B. Sosman [1] considers the allotropic changes in silica are partly structural and partly atomic, as described on p. 325. He regards the sluggish changes as due to the rearrangement of the silicon and oxygen atoms, and the rapidly reversible changes as due to changes in the atom and possibly in the relative positions of the atoms. He thus concludes that the α–β change in quartz is due to a change in the position of the oxygen atoms of adjacent pairs, which are pushed farther apart than they are in α-quartz and form vertical pairs,[2] and that tridymite and cristobalite are formed by the different orientation of the oxygen pairs which are linked with other atoms.

Cristobalite has a variable inversion temperature. Fenner has shown that the higher the temperature at which it is formed, the higher is its β–α inversion point. Sosman explains this by assuming that some of the oxygen atoms are in relatively fixed positions, whilst others rotate about the axis of the silica thread, this structure being maintained by rapid cooling to 200°–300° C.

R. B. Sosman considers that in β-cristobalite the threads of silica triplets lie parallel to the cube diagonal of an imaginary octahedron or perpendicular to the octahedral face, the oxygen atoms occurring in octahedral planes perpendicular to the axes of the threads, whilst in tridymite the threads lie parallel to the hexagonal axis, and each pair of oxygen atoms lies in a plane perpendicular to the thread-direction. Both this and the structure suggested by Beckenkamp probably necessitate the assumption of twinning to explain the dihexagonal symmetry of β-tridymite. There

[1] *Loc. cit.*, p. 327.

[2] As the pairs are close together in α-quartz, a fairly high temperature is necessary to alter their positions; whilst in the tridymite structure the oxygen atoms are farther apart, and consequently a lower temperature suffices to alter their positions. In α-cristobalite the distance between the oxygen atoms is intermediate between that of quartz and tridymite, as also is its inversion temperature.

is, however, at present no X-ray data regarding the structure of tridymite and cristobalite, so that until this is obtained no definite proof exists.

Sosman suggests that his theory of the constitution of silica might be extended to the constitution of silicates, as many of these show similar changes of density and stability.

Amorphous silica, when heated under suitable conditions, is changed into one of the crystalline forms. It may be converted into crystalline quartz by direct heating in the presence of a catalytic agent such as sodium tungstate, alkali-phosphate, lithium chloride, or sodium molybdate. It is possible that cristobalite and tridymite may also be formed during the heating. Thus, Fenner [1] found that chalcedony is first converted at 800° C., in the presence of a flux, into quartz and tridymite, the latter on further heating disappearing; but Washburn and Navias [2] consider that chalcedony is converted on heating partly into isotropic silica glass which later crystallises, forming cristobalite.

In the absence of a catalytic agent it is difficult to convert amorphous silica into the crystalline state, though the possibility of doing so has been shown by Kyropoulos and Braesco, and also by Fenner.

Fenner [1] found that when amorphous silica is heated without any flux to a temperature of 1030° C., it is changed completely in sixty-nine hours into cristobalite, but Houldsworth and Cobb [3] found that amorphous silica in the presence of 5 per cent. of soda is converted into cristobalite at 700° C. Another method by which amorphous precipitated silica may be converted into quartz, is to heat it to a temperature of 300°–400° C. with water under pressure and in the presence of a catalytic agent such as carbon dioxide, sodium carbonate, boron fluoride, or sodium silicate.

Quartz, when heated, is usually converted into a β-form at 575° C.; this form, when heated to a still higher temperature, changes into tridymite or cristobalite, according to the conditions of the experiment. The conditions under which these two modifications are formed are not clearly understood, but it is probable that tridymite is the stable form at the lower temperatures and cristobalite at a temperature nearer to the melting-point.

The conversion of quartz into other allotropic forms of silica may, according to Le Chatelier and B. Bogitch, be effected in three ways.

(*a*) By solution and subsequent crystallisation.

(*b*) By the action of heat and of any impurities present which can act as a catalyst.

(*c*) By the action of gases or vapours.

Several molten silicates are able to dissolve quartz at high temperatures, and recrystallisation takes place to a greater or less extent, with the formation of tridymite or cristobalite, according to the temperature and to the conditions of crystallisation. Thus, at 1200° C. tridymite may crystallise out, whilst by heating the material to 1500° C. some of the tridymite may be dissolved, and, if the melt is cooled rapidly, cristobalite may crystallise out. The crystallisation which occurs on cooling to only a small extent is due, according to Grum Grzmailo, to the fact that the molten fluxes

[1] *Amer. J. Sci.*, **36**, 380 (1913).
[2] *J. Amer. Cer. Soc.*, **5**, 565 (1922).
[3] *Trans. Eng. Cer. Soc.*, **21**, 258 (1921–22).

will dissolve quartz to a greater extent than tridymite and cristobalite, and the latter are, therefore, thrown out of solution to give place to the quartz. The more mobile the molten silicate in contact with the quartz grains, the more rapid is the solution and recrystallisation into cristobalite or tridymite; if the molten material consists of quartz dissolved in fused calcium silicates, the crystallisation on cooling slightly is so rapid that the quartz may be converted wholly into cristobalite, no tridymite being produced.

The presence of almost any base, but particularly of lime, is very useful in aiding the transformation of quartz into cristobalite or tridymite, the value of such a base depending on the fluidity of the molten silicate produced. Thus, Seaver found that 77 per cent. of a quartzite heated in the presence of lime was converted into cristobalite and tridymite, whilst only 48–95 per cent. was transformed when the same material was heated under the same conditions, but in the absence of lime. O. Rebuffat found that phosphoric acid was very effective in transforming quartz into cristobalite and tridymite. Scott gives the following catalytic agents in order of their effectiveness in aiding the transformation of quartz: iron oxide, lime, magnesia, titanic oxide, alumina.

The action of flue dust, according to Mellor and Emery, is also very noticeable in facilitating the conversion of quartz into low specific gravity forms of silica.

Gaseous vapours are often very effective in aiding the transformation of quartz into tridymite and cristobalite, their effect being often noticeable in the interior of articles where no solid matter could penetrate.

The rate at which the allotropic changes take place when quartz is heated depends upon (*a*) the size of the grains of silica; (*b*) the nature of any impurities which may be present, and their amount; (*c*) the temperature attained during the heating; and (*d*) the duration of heating. The effect of the size of the particles in the conversion of quartz into cristobalite and tridymite is shown in Table CVI, due to Seaver.

TABLE CVI.—*Effect of Grain-Size on Inversion of Silica*

	Percentage of Cristobalite formed by burning at 1450° C. for 40 hours.	
	Silica Bricks.	Coarsely Ground Quartz.
1 Firing . .	77·35	48·95
2 Firings . .	82·87	68·62
3 Firings . .	85·98	..

Ferguson and Merwin state that the lowest temperature at which quartz is changed into tridymite is 870° C. That the rate of conversion of quartz into tridymite depends upon the temperature, is shown by the fact that at a high temperature the conversion is far more rapid than at a lower temperature. At 1300° C. the transition is fairly

rapid, but below 1000° C. it is very slow. The rate of change is most rapid between 1410° and 1435° C.

The conditions governing the conversion of tridymite into cristobalite are by no means properly understood. It is generally considered that tridymite tends to form cristobalite at temperatures above 1470° C., though in steel-melting furnaces in which bricks are heated to a temperature considerably over 1470° C., cristobalite is frequently absent, even though it is supposed to form above this temperature. Bleininger and Ross found that the production of cristobalite occurs chiefly at the highest temperatures, and give the following figures in support of this statement :—

TABLE CVII.—*Formation of Cristobalite*

Temperature, ° C.	Cristobalite, per cent.
1350	57·13
1450	81·26
1500	90·00

Seaver found that quartz is converted almost wholly into cristobalite at 1630° C., very little tridymite being produced. He also found that repeatedly heating silica bricks at 1450° C. with a soaking period of forty hours caused the conversion of most of the quartz into cristobalite, but no tridymite was formed. Fenner considers that in the absence of a flux cristobalite always forms at a temperature of 1470° C., but if a flux is present tridymite may form. Day and Lacroix, on the other hand, have independently stated that cristobalite may be formed even in the presence of fluxes, such as lime, alumina, and iron oxides, which are supposed to favour the formation of tridymite, whilst Le Chatelier has found cristobalite in furnace linings containing as much as 10 per cent. of metallic oxides, and it is also found just below the metallic superficial coating of Bessemer converters. H. Le Chatelier considers cristobalite to be metastable at all temperatures below its fusing-point, and that it will revert to tridymite if conditions permit. He suggests that the conditions which favour the formation of cristobalite will, if continued sufficiently long, cause tridymite to form.

All forms of silica when heated to a sufficiently high temperature fuse and form amorphous silica glass, which is the final product of the effect of heat on silica. Thus, when heated under suitable conditions, quartz will pass through its various allotropic modifications and finally fuse, forming silica glass, but if the heating is very rapid the quartz may fuse without appearing to pass through the intermediate stages. Quartz fuses into silica glass at about 1500° C. Tridymite and cristobalite fuse respectively at 1670° C. and 1625° C.

When fused silica is cooled very slowly it will pass through the various allotropic modifications in the reverse order and finally form α-quartz, but under ordinary conditions the molten glass solidifies without crystallisation and forms amorphous silica glass. Cristobalite may, however, be produced by cooling fused silica to 1500° C., and maintaining it at that temperature for several hours. Similarly,

tridymite may be produced from fused silica by maintaining the material at 800° C. for twenty days, but in the presence of a catalytic agent the transformation is much more readily effected. Fenner states that, on cooling, cristobalite reverts to tridymite between 1470° C. and 870° C., though Foxwell states that the change may be so slow as not to occur under the usual conditions of cooling. Fused silica has never been converted into quartz merely by cooling slowly, but it has been effected by maintaining at a temperature beteeen 300° C. and 750° C. (in no case rising above 800°–870° C.) for a long period in the presence of a catalyst.

The relation of these various allotropic modifications of silica to each other has not yet been discovered. W. & D. Asch have suggested that the difference between them is due to the fact that they contain different numbers of atoms in their molecules, the number being in proportion to their specific gravities. Thus, as tridymite and cristobalite have lower specific gravities than quartz, they should have fewer atoms in their molecules. This has not been proved ; if it is correct the molecules or space-lattices must contain a very large number of atoms.

Further light on the constitution of the various allotropic forms of silica may be obtained by investigation with X-rays by Bragg's method. The structure of quartz is described on p. 327, but up to the present the relations between quartz and tridymite and cristobalite have not definitely been determined.

The Constitution of Silicic Acids and Silicates

Silicates are classed according to the ratio between the oxygen combined with the base and that combined in the acid radicles of the silicate, as shown in Table CVIII.

Table CVIII.—*Nomenclature of Silicates*

Acid Oxygen : Basic Oxygen.	Formula.		Metallurgical Name.	Mineralogical Name.
	RO Base.	R_2O_3 Base.		
Less than 1 .	$3RO\ SiO_2$	$R_2O_2\ 4SiO_2$	Subsilicate Basic silicate	.. ..
,, 1 .	$2RO\ SiO_2$	$2R_2O_3\ 3SiO_2$	Singulosilicate Monosilicate	orthosilicate.
,, 1·5 .	$4RO\ 3SiO_2$	$4R_2O_3\ 9SiO_2$	Sesquisilicate	..
,, 2 .	$RO\ SiO_2$	$R_2O_3\ 3SiO_2$	Bisilicate	metasilicate.
,, 3 .	$2RO\ 3SiO_2$	$2R_2O_3\ 9SiO_2$	Trisilicate	..
,, 4 .	$RO\ 2SiO_2$	..	Quadrisilicate	dimetasilicate.

Orthosilicates have a ratio of acid oxygen : basic oxygen of less than 1·5–1·7. Metasilicates have a ratio greater than 1·7. In the absence of alumina the dividing line between ortho- and metasilicates is always 1·7, but where alumina is present a

range of intermediate ratios occurs, as mentioned above, due to the alumina acting both as an acid and as a base.

The principal theoretical silicic acids from which silicates are formed, according to Clarke,[1] are :

		Oxygen Ratio.
Dimetasilicic acid	$H_2Si_2O_5$ or $H_2O\ 2SiO_2$	4 : 1
Trisilicic acid	$H_4Si_3O_4$ or $2H_2O\ 3SiO_2$	3 : 1
Metasilicic acid	H_2SiO_3 or $H_2O\ SiO_2$	2 : 1
Diorthosilicic acid	$H_6Si_2O_7$ or $3H_2O\ 2SiO_2$	1·33 : 1
Orthosilicic acid	H_4SiO_4 or $2H_2O\ SiO_2$	1 : 1

Some of these acids are unknown in nature as isolated substances, but there are many compounds which appear to be salts of them.

Orthosilicic acid has been prepared by passing silicon tetrafluoride into water, filtering the precipitate, and drying it by washing with benzene and then with ether.

If a solution of an alkali silicate is acidified with hydrochloric acid part of the silicic acid separates out as a gelatinous precipitate, but if the solution is very dilute the whole of the silicic acid remains in solution. The excess of acid and the sodium chloride may be separated by dialysis.

If colloidal silicic acid is evaporated *in vacuo* at 15° C. over sulphuric acid, a transparent glass is obtained corresponding to the metasilicate H_2SiO_3. An acid of this composition is also obtained by dehydrating precipitated silicic acid with 90 per cent. alcohol. The following examples will show the molecular composition of various natural silicates :—

Subsilicates (oxygen ratio, less than 1 : 1)—

Sillimanite	$Al_2O_3\ SiO_2$
Tricalcium silicate	$3CaO\ SiO_2$

Orthosilicates (oxygen ratio, 1 : 1)—

Forsterite	$2MgO\ SiO_2$
Fayalite	$2FeO\ SiO_2$
Calcium orthosilicate	$2CaO\ SiO_2$
Willemite	$2ZnO\ SiO_2$
Phenakite	$2BeO\ SiO_2$
Zircon	$ZrO_2\ SiO_2$

Many other orthosilicates also occur in nature.

Diorthosilicates (oxygen ratio, 1·33 : 1)—

Barysilite	$3PbO\ 2SiO_2$ or $Pb_3Si_2O_7$

Metasilicates (oxygen ratio, 2 : 1)—

Sodium metasilicate	$Na_2O\ SiO_2$ or Na_2SiO_3
Calcium metasilicate (Wollastonite)	$CaO\ SiO_2$ or $CaSiO_3$
Magnesium metasilicate (Enstatite)	$MgO\ SiO_2$ or $MgSiO_3$

Trisilicates (oxygen ratio, 3 : 1)—

Meerschaum	$2MgO\ 3SiO_2 2H_2O$

[1] *Bull. U.S. Geol. Survey*, 125 (1895).

Mixed silicates apparently composed of two or more single silicates, are fairly common. Such mixtures are termed (*a*) *crystalline isomorphous mixtures*; (*b*) *mixed crystals*; or (*c*) *solid solutions*; though the last term may include amorphous as well as crystalline substances (see also p. 300 and Chapter XI).

Isomorphous mixtures consist of crystals which contain more than one base (or of crystals in which the original base has been completely replaced by another) without altering the form of the crystal. Isomorphous mixtures are possible because the shape of a crystal does not depend wholly on its chemical composition, but on the number and mode of combination of the atoms. Hence, as found by Mitscherlich, the same number of atoms combined in the same manner, produce the same crystalline form, and, consequently, one atom or group of atoms may be replaced by another atom or group without altering the crystal form. Elements which replace each other in isomorphous crystals are characterised by equal valency or combining capacity. This enables different elements to enter into combination in the same crystal, or one element may be replaced by another without altering the form of the crystal, provided suitable elements are available. These isomorphous changes are sometimes important in the case of ceramic materials, as the crystals of the latter may be alike though the chemical composition is different. Thus, albite and anorthite felspars form apparently identical crystals when mixed in any proportion, and the melting-point of the various mixtures lies in a straight line connecting the melting-points of the extreme members of the series.

E. T. Wherry [1] considers that isomorphism is dependent more upon approximate equal volumes than upon equal valencies and chemical relationship. If correct, his suggestion would explain (*a*) the limited replaceability of potassium and sodium and the more complete replaceability of potassium and barium in the felspar group; (*b*) the significance of water in analcite; (*c*) the scarcity of potassium pyroxenes; (*d*) the presence of alkalies in the beryl group; (*e*) the excess of silica in the nephelite group; (*f*) the extensive isomorphism in the garnet group; (*g*) the replacement of lithium for iron and aluminium for magnesium in tourmaline; (*h*) the absence of (Ca, Na) and (SiO_4, Si_3O_8) replacements in the zeolite group; and (*i*) the absence of (SiO_4, Si_3O_8) replacements in micas.

Isomorphous crystals of different substances cannot be distinguished by inspection; consequently, ceramic materials which may be isomorphous must be carefully tested before use, or they may contain substances due to secondary replacement which may wholly unfit them for the purpose for which it is desired to use them. As a result of isomorphism it is extremely difficult to obtain some ceramic materials in a perfectly pure state, because most of the methods of purification only partially separate the undesirable substances. Thus, orthoclase—which is a potash-felspar—usually contains some sodium, whilst albite—which is a soda-felspar—usually contains some potassium. In Table CIX (due to Arzuni) an element in any series can usually replace or take the place of any other element in the same series.

[1] *Am. Mineral.*, 8, 1–8 (1923).

TABLE CIX.—*Isomorphous Elements*

Series I.	Hydrogen, potassium, rubidium, cæsium, ammonium, sodium, lithium, and silver.
Series II.	Beryllium, zinc, cadmium, magnesium, manganese, "ferrous" iron, nickel, cobalt, platinum, calcium, copper, strontium, barium, lead.
Series III.	Lanthanum, cerium, yttrium, erbium.
Series IV.	Aluminium, "ferric" iron, chromium, cobalt, manganese.
Series V.	Manganese, copper, mercury, lead, silver, gold.
Series VI.	Silica, titanium, zirconium, tin, lead, molybdenium, uranium, platinum, rhodium, iridium.
Series VII.	Nitrogen, phosphorus, vanadium, arsenic, antimony, bismuth.
Series VIII.	Niobium, tantalum.
Series IX.	Sulphur, selenium, chromium, manganese, nitrogen, arsenic, antimony.
Series X.	Fluorine, chlorine, bromine, iodine, manganese.

Note.—The same element may appear in two or more series.

Thus, to take an example from Series II, gehlenite, $3CaO\ Al_2O_3\ 2SiO_2$, is a definite crystalline mineral, yet the calcium in it can be replaced by "ferrous" iron, magnesium, strontium, barium, or copper, and apparently by any other element in the series without altering its crystalline form. The same substance illustrates Series IV, as the alumina in it may be replaced by ferric iron, chromium, cobalt, or manganese without altering the physical properties of the crystals.

If the replacement or substitution involves several elements, it is easy to understand from Table CIX why many natural silicates have extremely complex and variable compositions, yet, in spite of this, each constituent atom occupies a definite position or portion of the space occupied by the molecule.

It is not necessary that the crystalline form should be completely identical in order that isomorphous replacement may occur. Federov has shown that each substance has its individual crystalline form, the angles of which differ—often only to a trifling extent—from those of other substances. Provided the shape of the crystals does not differ greatly, isomorphism is possible.

The formula of an isomorphous mixture or of a mass of "mixed" crystals is sometimes written by collecting in brackets all the elements which can replace each other without altering the crystalline form. Thus, what may appear on analysis to be a very impure iron carbonate, containing calcium, manganese, and magnesium, carbonates may also be regarded as a complex isomorphous mixture with the formula $(Fe, Ca, Mn, Mg)\ CO_3$. The elements in brackets may be in any proportions. This use of a formula is not strictly correct (especially if it involves the use of fractions), but it is very convenient and often instructive (see p. 310).

Mixed Crystals.—Substances of different crystal form can only combine in fixed

proportions, but those of the same or sufficiently similar crystalline form can be mixed in any proportions. Mixed crystals only differ from isomorphous mixtures in their origin, the term mixed crystals being usually confined to isomorphous crystals produced from a mixture of different substances, whilst the term " isomorphous crystals " is also used to include substances in which one element has been completely replaced by another or to relate to two or more different substances, all of which have the same crystalline form.

The structure of mixed crystals appears to consist of separate layers of each kind of crystal, and their properties are largely additive and characteristic of mixtures rather than of compounds. For instance, when reacting with a base, one replaceable element appears to be more seriously attacked than another, though some silicates which are regarded as mixed crystals appear to act as definite chemical compounds.

Solid solutions are substances which appear to be solid and homogeneous, but are really mixtures. They may be regarded as two-phase systems, one being the solute, or substance in solution, and the other the solvent. If such substances are crystalline, they are known as " mixed crystals," but if amorphous—as glazes, glasses, and various vitrified materials—the term " solid solution " is usually employed. Many silicates appear to be " solid solutions " ; when their constituents are melted together they do not form mixed crystals on cooling, but usually form a non-crystalline vitreous mass or glass. Most single silicates, if fused, readily crystallise when cooled slowly, but mixtures of two or more silicates only crystallise with difficulty. Complex mixtures of silicates seldom crystallise, but remain in the vitreous state. Consequently, when it is desired to prepare a glaze or other vitreous substance, it is always desirable to make its composition somewhat complex, by mixing several silicates or several substances which will form a mixture of silicates. Mixtures corresponding to exactly whole numbers in chemical formulæ are avoided for the same reason—complex glasses and glazes being less likely to crystallise or " devitrify " than those which are much simpler in composition.

Hydrous Silicates.—Many crystalline silicates lose water when heated, and are, therefore, known as hydrous or hydrated silicates. The elements (hydrogen and oxygen) which produce this water may be present in silicates in one or more of three forms, known as (*a*) colloidal water ; (*b*) water of constitution ; and (*c*) water of hydration or water of crystallisation, the first and last being the most weakly combined and most readily removable.

The *colloidal water* in a substance is present in indefinite proportions. It is removed continuously and fairly steadily when the substance is dried and gives no indication of being definitely combined. This is a characteristic of many colloidal gels, including colloidal silica and colloidal alumina ; it is also a well-known characteristic of plastic clay pastes. Some of the iron hydroxides in clay also appear to contain water of this type. When only the " colloidal water " (sometimes termed the " water of plasticity ") is removed, the plasticity of the material may be restored by mixing it with a suitable quantity of water and allowing it to stand or " sour " (p. 274) until that water is uniformly distributed. If the clay has been dried at too high a temperature, so that some of the " water of constitution " is also driven off, the

plasticity of the clay cannot be fully restored. E. Lowenstein found that, when dried at 25° C. over sulphuric acid, clay lost up to one-quarter of its " water of constitution," as well as the whole of its " colloidal water " and moisture. This has been confirmed by Mellor, Sinclair, and Devereaux,[1] who found that the water in halloysite was most easily removed, that in ball clay being much less readily affected, and that in china clay being only slightly affected. When exposed to a moist atmosphere the loss of colloidal water is restored by absorption.

The *water of constitution* appears to be a definite part of the molecule, though it does not exist therein as " water," but usually in the form of *hydrogen*, attached to one or more parts of the molecule and of *hydroxyl* (OH) groups attached to the molecule, but not directly to the hydrogen. In such cases, water is only formed when the molecule is partially decomposed. For instance, when an almost " pure " clay is heated to 600° C. it evolves about 13 per cent. of water, which appears to have been formed by the partial (or possibly complete) decomposition of the clay-molecule.

According to W. and D. Asch, who employed very elaborate formulæ, the elements of the water of constitution in clays and some alumino-silicates may be attached either to the basic or to the acid radicles of their equivalents in the formula, or to both of these simultaneously. What they term the " acid water " may also be attached to either the alumina or to the silica group or " ring," in a manner analogous to the distribution of the same elements in complex aromatic organic compounds.

When the water of constitution is removed, the original substance cannot be reproduced merely by the addition of water under favourable conditions, as is often the case when colloidal water or water of crystallisation is removed. Mellor and Holdcroft found that dehydrated china clay, when heated to 300° C., under a pressure of 200 atmospheres, only absorbed 2·5 per cent. of water, whilst Rieke was only able to effect the recombination of 1·1 per cent. of water in a calcined Bohemian kaolin. Laird and Geller,[2] on the contrary, found that if the clay had not been heated to a temperature higher than 700° C., it could be rehydrated to some extent by heating for 8–48 hours at a temperature of 200–250° C. in an autoclave. If the clay has been heated higher than 700° C., the rehydration is correspondingly more difficult.

The *water of crystallisation* or *water of hydration* is that which is evolved when substances of a crystalline nature are heated to a low temperature. It differs from " water of constitution " inasmuch as the original substances can be reformed by dissolving the heated substance in water and then allowing it to recrystallise, whereas " water of constitution " cannot be so restored.

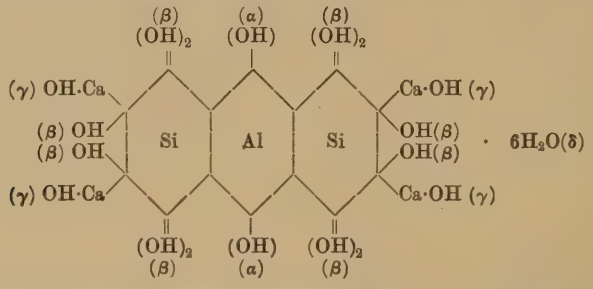
The precise manner in which the atoms comprising the water of crystallisation are united to those forming the remainder of the substance has never been definitely ascertained, but the bond appears to be a very loose one and quite different in character from that of the water of constitution.

Sometimes a silicate will form different kinds of crystals with different amounts of water of crystallisation, *e.g.* sodium silicate occurs in three crystalline forms :—

[1] *Trans. Eng. Cer. Soc.*, **21**, 104 (1921–22).
[2] *J. Amer. Cer. Soc.*, **2**, 828 (1919).

Formula.	Crystalline Form.
$Na_2SiO_3 9H_2O$ . . .	rhombic.
$Na_2SiO_3 6H_2O$ . . .	monoclinic.
$Na_2SiO_3 4H_2O$ . . .	hexagonal.

W. and D. Asch have devised the following illustration to show the various ways in which the water may be present :—



where α represents hydroxyl groups associated with the alumina ring, β hydroxyl groups associated with the silica ring, γ hydroxyl groups associated with the base, and δ is the " water of crystallisation."

If the above formula truly represents the constitution of the material so represented it is obvious that each of these four hydroxyl groups would possess different properties. Unfortunately, such highly complex alumino-silicates are so difficult to deal with—chiefly on account of their inertness and insolubility—that it has not, hitherto, been possible to make much progress in this direction. J. Thugutt [1] has found one-third of the alumina in sodium nepheline hydroxide behaves differently from the remainder. He also observed the same difference in the case of kaolin. P. Silber [2] found that the sodium attached to the aluminium in some alumino-silicates is separated by gaseous hydrochloric acid, but that associated with the silica is not affected. In both cases, if a structural formula similar to that on p. 346 is used, it will be seen that two-thirds of the soda will be combined with the silica and one-third with the alumina, so that it is quite natural that one-third should behave differently from the rest. Clays and some alumino-silicates behave curiously with regard to parting or recombining with water. When the water is that described on p. 336 as " colloidal water," or that described on p. 337 as " water of crystallisation," its removal and recombination are usually fairly simple, but the matter is quite different as regards the " water of constitution." The latter can only be replaced (if at all) by elaborate methods of synthesis, in which the original constitution of the molecule is rebuilt by indirect means. Hence, if a clay is heated to a temperature at which it loses part of its water of constitution, the essential properties of the clay cannot be restored by any simple treatment with water, no matter how severe such treatment may be.

The power possessed by such a material of recombining with water depends on :

(*a*) The manner in which the atoms previously associated with the lost hydroxyl groups can be attacked without completely destroying the structure of the molecule.

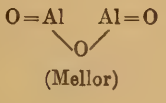
[1] *N. Jahrb.*, **9**, 557 (1894–5).

[2] *Ber. d. Deutsch. Chem. Ges.*, **14**, 941 (1881).

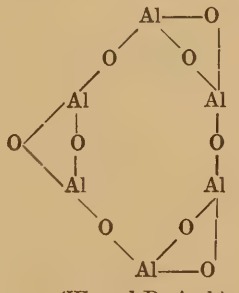
(*b*) The solubility of the product and the ease or difficulty with which it will react with other substances. Unfortunately, most ceramic materials are extremely difficult to deal with in this respect.

The Constitution of Alumina and its Hydroxides

Alumina is usually represented by the formula Al_2O_3, but it is most probable that its formula is a multiple of this, especially when in combination with other materials, though its molecular weight in the solid state has never been determined. The graphic formulæ suggested by J. W. Mellor and by W. and D. Asch respectively, are as follows :—



(Mellor)



(W. and D. Asch)

Rankin and Merwin [1] claim to have identified two allotropic forms of alumina : the α-form which is found in Nature as corundum and a β-form produced at high temperatures whose precise relation to the α-form is not, as yet, known. The β-form is regarded as a polymerised form containing a much larger number of atoms in the molecule than are present in the α-form. The temperature at which this polymerisation or change in constitution occurs does not appear to have been definitely ascertained. Houldsworth and Cobb,[2] and Wholin, suggest a temperature of 1060°–1130° C., but Keppeler [3] has reported its occurrence at about 750° C., viz., at the temperature at which the maximum shrinkage of dried precipitated alumina occurs. Mellor [4] suggests a temperature of just over 800° C.

There appear to be three distinct types of aluminium hydroxides :—

(i) The *Diaspore type*, which occurs near Var and Hérault, in the south of France. This type contains 12–14 per cent. of water, and has a formula approximating to $H_2Al_2O_4$ or $Al_2O_3H_2O$.

(ii) The *True Bauxite type*, which is found at Les Baux, in France ; it contains 20–24 per cent. of water, and appears to correspond to $H_4Al_2O_5$ or $Al_2O_32H_2O$.

(iii) The *Hydrargillite or Gibbsite type*, which contains 27–35 per cent. of water, and corresponds to $H_6Al_2O_6$ or $Al_2O_33H_2O$.

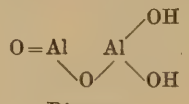
Cornu and Redlich [5] consider that there are only two hydroxides, and that the dihydrate bauxite is a mixture of these.

[1] *J. Amer. Chem. Soc.*, **38**, 568–88 (1916).
[2] *Trans. Eng. Cer. Soc.*, (Oct. 1922).
[3] *Keram. Rund.*, **21**, 307 (1913).
[4] *Trans. Eng. Cer. Soc.*, **10**, 94 (1910–11).
[5] *Zeit. f. Chem. u. Ind. der Kol.*, **4**, 90 (1908).

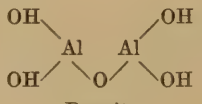
Aluminium hydroxides containing other proportions of water are also found, but their composition appears to be very variable. They are probably mixtures of diaspore ($Al_2O_3H_2O$) and bauxite ($Al_2O_32H_2O$), especially as R. Wohlin found that some of these materials, when heated, lose their "combined water" at two different temperatures. Bigot has found that the aluminium hydroxides which contain more than 14 per cent. of combined water lose it in two stages, but those which contain less than 14 per cent. of such water lose it almost entirely at some temperature above 500° C.

Houldsworth and Cobb [1] have found that some grey bauxite has four critical ranges of temperature :—

(*a*) Below 180° C. ; (*b*) 300°–365° C. ; (*c*) 510°–620° C. ; and (*d*) 940°–965° C. In the last stage heat is evolved, the change being exothermal in character. The two ranges (*b*) and (*c*) are those at which the water of constitution is evolved. The arrangement of the atoms in these hydroxides has never been accurately determined. The constitutional formulæ generally accepted are :



Diaspore



Bauxite

No satisfactory simple formula for hydrargillite has been found, but Mellor has suggested the formula for gibbsite.

Alumino-Silicates

A very large and important class of ceramic materials—including the clays and felspars—contain both alumina and silica as well as water, and many theories have been advanced regarding their constitution. It is comparatively easy to obtain clean and pure crystals of felspar and some other compounds of silica and alumina with a metallic oxide, but the physical properties of clays are such as to make it a matter of extreme difficulty to obtain specimens which are sufficiently pure to be used in the determination of their chemical constitution.

This is partly due to (i) the complexity of the materials ; (ii) their general inertness at temperatures below 600° C. ; (iii) the ease with which they appear to be completely broken down into simple substances (such as silica, alumina, and water) at high temperatures ; and (iv) the apparent impossibility of producing readily soluble salts corresponding to the acids.

In order to make clear some of the difficulties involved in investigating the chemical constitution of clays, felspars, and allied materials, some of the more important theories on the subject may be briefly described.[2]

1. The theory that *alumino-silicates are essentially salts of a silicon hydroxide, in which the hydrogen is partly replaced by aluminium and partly by other metals*, cannot be correct, because (i) the percentage of silica varies, whilst the ratio of alumina : base

[1] *Loc. cit.*, p. 339.

[2] The subject is discussed at much greater length in *The Silicates in Chemistry and Commerce*, by W. & D. Asch (Constable).

remains constant, and (ii) the hydrogen in the supposed hydroxide cannot be entirely replaced by a single metal, neither can the requisite complex hydroxides be prepared and alumino-silicates reproduced from them.

2. The theory that *alumino-silicates are double salts of aluminium and other metals and are also isomorphous mixtures of these double salts*, as suggested by Berzelius and later by Smithson, cannot be correct, because reactions may occur in which the proportion of silica varies, whilst the ratio of the alumina : base remains constant. Moreover, it does not appear possible to produce any such alumino-silicates by the interaction of the hypothetical constituent salts as can be done in the case of other (true) double salts. Thus, the action of Na_2SiO_3 upon $Na_2Al_2O_4$ does not produce a double salt of these two substances, but analcime, $Na_2OAl_2O_34SiO_22H_2O$, in which there is a larger proportion of silica than would occur in a true double salt.

3. The theory that *alumino-silicates are molecular compounds, i.e.* composed of various chemical compounds which have nothing in common as regards their chemical nature, but are loosely held by some unknown bond, is highly improbable, because such compounds must be very easily decomposed, whereas the felspars and analogous alumino-silicates are only decomposed with great difficulty. Some alumino-silicates are highly stable substances and may be dissolved and recrystallised without change, and when decomposed they split up into other complex substances and not into the individual molecules of which this theory assumes they consist.

4. The theory that *alumino-silicates are isomorphous mixtures of silicic and aluminic acids*, and

5. The theory that *clays are mixtures of mutually precipitated colloids*, are not capable of definite proof on account of the experimental difficulties involved in the artificial preparation of such materials. The second of these theories appears to be improbable, because such precipitated colloids ought to be readily decomposed by liquid chemical reagents, whereas clays are stable at temperatures below 600° C. Moreover, mutually precipitated colloidal alumina and silica does not possess some of the essential properties of clay.

6. The theory that *alumino-silicates are double salts of silicic and aluminic acids or isomorphous mixtures of these double salts* is a modification of the fourth theory and is equally unsatisfactory, as it does not account for the invariable presence of both alumina and silica in the decomposition and reaction products. Moreover, unless the term " double salts " is extended in an undesirable manner to include " double acids " free from bases, this theory makes an unnecessary and improper distinction between compounds consisting only of alumina and silica and the alumino-silicates, whereas it is generally agreed that there is a very intimate relationship between them.

7. The theory that *alumino-silicates are composed partly of complex alumino-silicic acids and partly of salts of these acids* is more nearly correct than the preceding ones, but it is unnecessarily complicated and does not fit the essential facts. The behaviour of artificially prepared mixtures of other complex acids and their salts does not correspond with the behaviour of clays and of the more clearly defined alumino-silicates.

8. The theory that *clays are alumino-silicic acids and that felspars and allied*

minerals are the normal salts of these acids is the only theory so far propounded which meets most of the facts, and it appears to do so in a simple and natural manner. Accepting this theory, the various minerals containing silica and alumina may be arranged as suggested by J. W. Mellor [1] on p. 345.

In all these compounds the alumina and silica act together as a complex radicle and not as two independent groups.

The alumino-silicic acids and their derivatives may be classified in three groups.

(*a*) *Alumino-silicic anhydrides*, which may be regarded as derived from the corresponding acids by loss of water. The typical formula for this group is $Al_{2x}Si_2O_{3x+2y}$ or $xAl_2O_3ySiO_2$, to which correspond such minerals as andalusite, chiastolite, kyanite, and sillimanite.

(*b*) *Alumino-silicic acids*, including clays and clay-like materials, the compositions of which are shown on pp. 343–352.

(*c*) *Salts of alumino-silicic acids*, which are sub-divided according to the proportion of base present and the ratio of alumina : silica.

The following minerals are typical of the groups in which they are placed :—

Alumino-monosilicates—	
Augite	$MgOAl_2O_3SiO_2$.
Chlorite	$2MgOAl_2O_3SiO_22H_2O$.
Alumino-disilicates—	
Anorthite felspar	$CaOAl_2O_32SiO_2$.
Celsian felspar	$BaOAl_2O_32SiO$.
Muscovite mica	$K_2O3Al_2O_36SiO_22H_2O$.
Zoisite	$4CaO3Al_2O_36SiO_2H_2O$.
Scapolite	$4CaO3Al_2O_36SiO_2$.
Alumino-trisilicates—	
Natrolite	$Na_2OAl_2O_33SiO_22H_2O$.
Alumina garnets	$ROAl_2O_33SiO_2$.
Lepidolite	$KLiOAl_2O_33SiO_2$.
Biotite	$KHO2MgOAl_2O_33SiO_2$.
Alumino-tetrasilicates—	
Spodumene	$Li_2OAl_2O_34SiO_2$.
Laumonite	$CaOAl_2O_34SiO_24H_2O$.
Leucite	$K_2OAl_2O_34SiO_2$.
Analcime	$Na_2OAl_2O_34SiO_22H_2O$.
Glaucophane	$Na_2OAl_2O_34SiO_2$.
Alumino-pentasilicates—	
Chabazite	$CaOAl_2O_35SiO_27H_2O$.
Harmotime	$BaOAl_2O_35SiO_26H_2O$.
Alumino-hexasilicates—	
Orthoclase felspar	$K_2OAl_2O_36SiO_2$.
Albite felspar	$Na_2OAl_2O_36SiO_2$.

[1] *Loc. cit.*, p. 339.

The groupings just mentioned do not indicate the arrangement of the atoms relative to one another in the alumino-silicic acid. This is a matter of great difficulty, and no agreement upon it has yet been reached.

Two widely differing sets of theories have been proposed.

(*a*) The theories based on the idea that alumino-silicic acids are " chain compounds " analogous to some organic acids.

(*b*) The theories based on the idea that alumino-silicic acids are " ring compounds " analogous to benzene and its derivatives.

The objection to the first group of theories is that they do not explain the partial replacements of hydrogen and of aluminium by other metals, nor do they account for the remarkable stability and general inertness of the alumino-silicic acid radicle. Those who maintain the correctness of a theory belonging to the first group, object that the conception of alumino-silicic acids as ring compounds is " fantastic " and " a mere juggling with formulæ." Yet no " chain formulæ " yet devised has enabled the prediction of so many properties as have been made by the use of the " ring formulæ " proposed by W. and D. Asch, nor do the chain formulæ agree with so many of the facts. Unfortunately, W. and D. Asch failed to realise the importance of using pure substances when calculating some of the formulæ on which their theory of ring compounds is based, and in several instances they have been so unwise as to propound explanations without adequate knowledge of the facts. The result has been that the importance of the essentials of their theory has been overlooked and the theory itself has been needlessly encumbered with complexities.

The whole subject requires a further large amount of investigational work before any single theory can be accepted, as showing the true constitution of the alumino-silicic acids.

The Constitution of Clays

The chemical constitution of clay has not been satisfactorily determined, though it has been the subject of many investigations and theories. It is comparatively easy to separate a large proportion of sand and silt from most samples of clay merely by mixing them with water and allowing the sand and silt to settle whilst the clay remains in suspension. Other methods may also be used for separating the finest particles of felspar, mica, and other materials, but whatever method of purification is used the final product—commonly known as *clay-substance* and sometimes as *true clay*—is seldom sufficiently definite in its characteristics to be regarded as a pure chemical compound. Common clays, and to a smaller extent china clay, are simply indefinite mixtures of some material conveniently termed " clay-substance " of unknown composition with other minerals such as quartz, felspar, mica, etc., so that any consideration of the chemical constitution of clay must be based on that of the " clay-substance " obtained by separating all the materials which are " not of the nature of clay." In some natural clays, the proportion of " clay-substance " appears to be very large, *e.g.* in the fireclays, and as far back as 1863, C. Mene suggested that the Alsatian fireclays were definite chemical compounds and not merely indefinite mixtures, but later investigations have shown that they are by no means free from

admixtures. Probably the purest clays obtainable commercially are some of the finest qualities of Cornish china clay, some of which appear to contain 95 per cent. or more of " clay-substance."

It is now generally agreed that whilst the " clay-substance " obtained from various kinds of clay is by no means constant in composition, yet in all cases it is chiefly composed of one or more substances which may best be described as alumino-silicic acids, though, as explained previously, their acid properties are not appreciable at ordinary temperatures. Hence, a convenient—and on the whole fairly correct—definition of clay is that it is " a naturally occurring material whose composition corresponds to that of an alumino-silicic acid mixed with an indefinite amount of sand and other minerals, the whole producing a mass which becomes plastic when mixed with a suitable quantity of water."

In considering the constitution of clay, the fact must not be overlooked that many clays are chiefly valued because of their plasticity, but as this is a physical and not a chemical property, it may be possessed by materials of very different chemical composition. For the same reason, the colloidal nature of some clays does not affect a consideration of the chemical constitution of the clay molecule (assuming one to exist), as colloidal properties are almost wholly of a physical nature. Consequently, the commercial uses of many clays are largely independent of their chemical composition and are chiefly due to the physical characters of the material. This fact, and the probability that clays have been derived from many minerals (and not merely from felspar), explains the differences in the chemical composition of " clay-substance " obtained from different sources. Yet when obvious impurities in the clay-substance have been eliminated or allowed for, the constancy of composition of the final product is truly remarkable.

Physically, the purest specimens of clay-substance yet obtained appear to consist of a mass of crystals—each so small as to be invisible, so that their crystalline nature can only be recognised by means of their X-ray spectrum—these crystals being interlocked with each other to form extremely minute " crumbs " which, when suitably moistened, have the structure of a colloidal gel, which is saturated with and surrounded by water held by intermolecular attraction and surface tension. The chemical properties of such a structure are almost wholly dependent upon the nature of the interlocked crystals which form the bulk of the dry mass, and it is these crumbs of interlaced, yet invisible crystals, which are the " true clay " or " clay-substance." As the purest form of clay-substance appears to be that derived from carefully prepared china clay or kaolin, it is important to observe that an analysis of this substance corresponds almost exactly to $H_4Al_2Si_2O_9$, which is the formula of the crystalline mineral kaolinite, and it is by no means impossible that this is identical with pure clay-substance, the only difference being of a physical nature due to the larger size of the crystals of kaolinite. It is sometimes assumed, though without sufficient evidence, that the clay-substance or essential constituent of *all* clays is identical with kaolinite and has the formula $Al_2O_32SiO_22H_2O$ or $H_4Al_2Si_2O_9$, but this cannot be correct, as the analyses of the most carefully purified clay-substance obtained from different clays show that a substance of this composition is not always

the chief constituent. It must suffice at present to state that whilst all clays appear to consist essentially of one or more alumino-silicic acids, they do not all consist of one such acid. On the contrary, several distinct alumino-silicic acids appear to be present in some clays.

This is confirmed by some investigations started by the author in 1909 and still not completed, in which clay-substance of various origins was heated with concentrated solutions of caustic soda and other hydroxides and oxides to various temperatures at different pressures up to 100 lb. per square inch for a considerable time and then cooled very slowly. The resulting crystalline products had all the characteristics of definite salts of different alumino-silicic acids, some of which have been separated and identified. W. Pukall has also obtained a complex alumino-silicate ($8Na_2O.6Al_2O_3.12SiO_2.12H_2O$) by heating kaolin with sodium chloride, thus showing the existence of an alumino-silicic acid corresponding to the formula $6Al_2O_3.12SiO_2.20H_2O$ in the kaolin he examined.

Unfortunately, " clay-substance " reacts so feebly at low temperatures, and is so easily decomposed at temperatures below which it becomes active, that it is extremely difficult to obtain definite alumino-silicates which can only have been produced by the simple combination of the acid with a base. Arguments founded on the products obtained by fusion are of little use unless it can be proved that the clay has not been decomposed prior to fusion.

The alumino-silicic acids, including those which occur in clays, have been classified by Mellor [1] as follows :—

Alumino-monosilicic acid (allophanic type) .	$Al_2O_3SiO_2xH_2O$.
Alumino-disilicic acid (kaolinitic type) . .	$Al_2O_32SiO_2xH_2O$.
Alumino-trisilicic acid (natrolitic type) .	$Al_2O_33SiO_2xH_2O$.
Alumino-tetrasilicic acid (pyrophyllitic type).	$Al_2O_34SiO_2xH_2O$.
Alumino-pentasilicic acid (chabazitic type) .	$Al_2O_35SiO_2xH_2O$.
Alumino-hexasilicic acid (felspathic type) .	$Al_2O_36SiO_2xH_2O$.

The more important minerals corresponding to these types are :

Allophane	$Al_2O_3SiO_2H_2O$.
Kaolin	$Al_2O_32SiO_22H_2O$.
Halloysite	$Al_2O_32SiO_22H_2O$.
Rectorite	$Al_2O_32SiO_2H_2O$.
Newtonite	$Al_2O_32SiO_25H_2O$.
Natrolite	$Al_2O_33SiO_2H_2O$.
Pyrophyllite	$Al_2O_34SiO_22H_2O$.
Montmorillonite	$Al_2O_34SiO_2H_2O$.

Among other alumino-silicic acids not included in Mellor's list are :

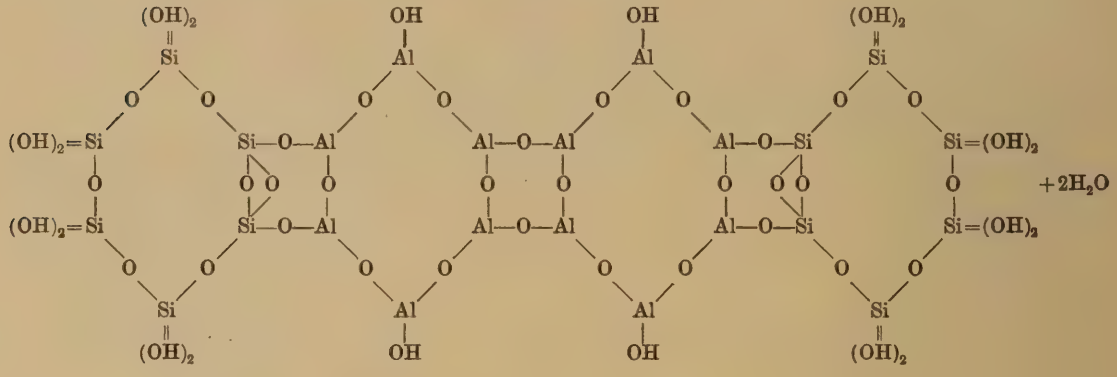
Cimolite	$2Al_2O_39SiO_23H_2O$
Collyrite	$2Al_2O_3SiO_29H_2O$.
Schrotterite	$8Al_2O_33SiO_23OH_2O$.

[1] *Loc. cit.*, p. 339.

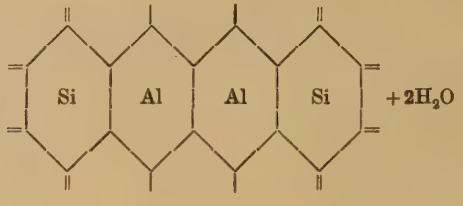
If attention is confined to the kaolinitic group, which appears to be the most important, several possible formulæ are devisable if the relative arrangement of the atoms are to be shown. The generally accepted formulæ $H_4Al_2Si_2O_9$ and $Al_2O_3 2SiO_2 2H_2O$ do not show this arrangement.

The subject has been examined very fully by W. and D. Asch,[1] who maintain that the minimum formula is $H_{24}Al_{12}Si_{12}O_{54}$, the silica, alumina, and oxygen atoms being arranged in four adjacent "rings," with hydrogen atoms attached. As explained on p. 343, the published objections to this theory of the constitution of kaolin have no scientific value, and as W. and D. Asch have succeeded in showing that no other formula hitherto published will fit all the known facts, their formula can scarcely be abandoned until a more satisfactory one is forthcoming.

Aschs' graphic formula for kaolinite is as follows :—



This may be simplified as suggested by the authors to—



or even to

$$\overset{\blacktriangle}{Si} \cdot \overset{\blacktriangle}{Al} \cdot \overset{\blacktriangle}{Al} \cdot \overset{\blacktriangle}{Si}$$

where $\overset{\blacktriangle}{Si}$ represents the silicon-oxygen hexagonal "ring" shown in the kaolinite formula and $\overset{\blacktriangle}{Al}$ the alumina-oxygen "ring." $\overline{Si}$ and $\overline{Al}$ represent corresponding pentagonal rings which appear to be necessary in calculating the formulæ of some clays.

[1] *The Silicates in Chemistry and Commerce* (Constable).

According to W. and D. Asch, the chief types of clay formulæ are as follows :—

(*a*) $\overset{\Delta}{Si}\ \overset{\Delta}{R}\ \overset{\Delta}{Si}$ which corresponds to $3Al_2O_3 12SiO_2 x H_2O$.

(*b*) $\overline{Si}\ \overset{\Delta}{R}\ \overline{Si}$,, $3Al_2O_3 10SiO_2 x H_2O$.

(*c*) $\overset{\Delta}{R}(—\overset{\Delta}{Si})_3$,, $3Al_2O_3 18SiO_2 x H_2O$.

(*d*) $\overset{\Delta}{R}(—\overline{Si})_3$,, $3Al_2O_3 15SiO_2 x H_2O$.

(*e*) $\overset{\Delta}{Si}\ \overline{R}\ \overline{R}\ \overset{\Delta}{Si}$,, $6Al_2O_3 12SiO_2 x H_2O$.

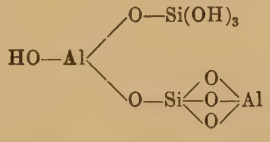
(*f*) $\overset{\Delta}{Si}\ \overline{R}\ \overline{R}\ \overset{\Delta}{Si}$,, $5Al_2O_3 12SiO_2 x H_2O$.

(*g*) $\overset{\Delta}{Si}\ \overset{\Delta}{R}\ \overset{\Delta}{Si}\ \overset{\Delta}{R}\ \overset{\Delta}{Si}$,, $6Al_2O_3 18SiO_2 x H_2O$.

(*h*) $\overline{Si}\ \overset{\Delta}{R}\ \overset{\Delta}{Si}\ \overset{\Delta}{R}\ \overline{Si}$,, $6Al_2O_3 16SiO_2 x H_2O$.

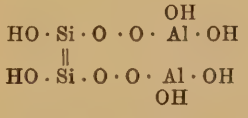
(*i*) $\overset{\Delta}{Si}\ \overline{R}\ \overset{\Delta}{Si}\ \overline{R}\ \overset{\Delta}{Si}$,, $5Al_2O_3 18SiO_2 x H_2O$.

Unfortunately, these formulæ are based on the chemical analyses of crude clays, some of which contain free silica in the form of quartz, and to that extent the formulæ are incorrect. When special efforts have been made to remove all impurities from natural clays the chemical composition of the residual " clay-substance " does not, in all cases, correspond to kaolinite, but more closely resembles some of the other formulæ just mentioned. The chief objection to most of the simpler formulæ is that they do not explain the action of various metallic oxides on clay or the behaviour of clay on heating. There is still some uncertainty as to the effect of heat on the china clay molecule, but, assuming for the moment that it is decomposed with the formation of free silica, free alumina, and free water (steam), any graphic formula ought to show the atoms arranged in such a manner that these three substances would be the probable product of dissociation. This is not the case with F. W. Clark's formula :



which is unsymmetrical and typical of a readily decomposable substance, whereas clay is largely inert and stable.

Pukall's formula :

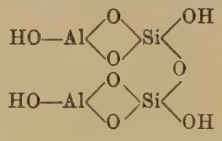


is symmetrical, but, as pointed out by Singer,[1] the double silica bond, like the double carbon bond in organic compounds, would be a source of weakness, so that this formula

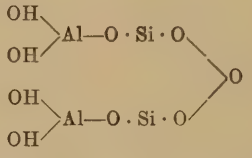
[1] *Sprechsaal*, **44**, 52–4 ; *Chem. Centrabl.*, **1**, 967 (1911).

suggests a readily decomposable compound with H_3AlSiO_5 as the most likely product, though no such compound is known and there are several reasons why it is not likely to be formed. The complete dissociation of a substance with Pukall's formula into silica, alumina, and water is difficult to understand, and the same remark applies to all chain formulæ in which the two atoms of silica are shown united by a double bond.

If a chain formula must be adopted, that of K. Haushofer,[1]



or the very similar one suggested by Mellor and Holdcroft [2] as a modification of Groth's formula,



appear to be the least objectionable, though both these formulæ suggest that the substances produced when the clay is dissociated would be H_2AlSiO_5 and H_2AlSiO_4 rather than silica, alumina, and water. With Asch's formula, on the contrary, the general stability and inertness of clay may be expected, and its decomposition first into two simple hydroxides and then into three simple oxides is what would be anticipated. There is a further objection to Groth's and similar formulæ, inasmuch as they represent the alumina as having a basic nature, whereas clays do not behave as aluminium salts, but as complex (alumino-silicic) acids.

The arrangement of those atoms of hydrogen and oxygen in clays which are evolved when a clay is heated (*i.e.* the so-called water of constitution) has been the subject of much speculation. Their positions in the simpler formulæ are shown on pp. 336–337, but the complex ring formulæ devised by W. and D. Asch permit a more symmetrical distribution of these elements among the alumina and silica atoms (see p. 338).

The Chemical Constitution of Burned or Calcined Clay

The difficulties experienced in finding a satisfactory formula to express the chemical constitution of raw clay are no greater than those experienced in investigating the nature of calcined or "burned" clay. Indeed, there is justification for the remark that the chemical constitution of clay which has been heated to redness is quite indeterminable. The effect of heat on clay is by no means clearly understood, and though there is evidence that the products obtained by heating the purest procurable china clay to 600°–1000° C. are free silica, free alumina and water, the last-named escaping as steam, it is by no means certain that this is the case, and the

[1] *Die Constitution der Naturlichen Silicate*, 1874.

[2] *Loc. cit.*, p. 339.

products when other clays are heated are so complex as to be beyond present-day methods of investigation.[1]

G. Shearer [2] found, on making an examination of the X-ray spectrum, that—

(i) When clay is heated and loses its "combined water," it loses its internal crystalline structure and gives no spectrum, but the nature of the amorphous matter is not revealed.

(ii) A new crystalline substance (not sillimanite) appears to be formed at about 1000° C.

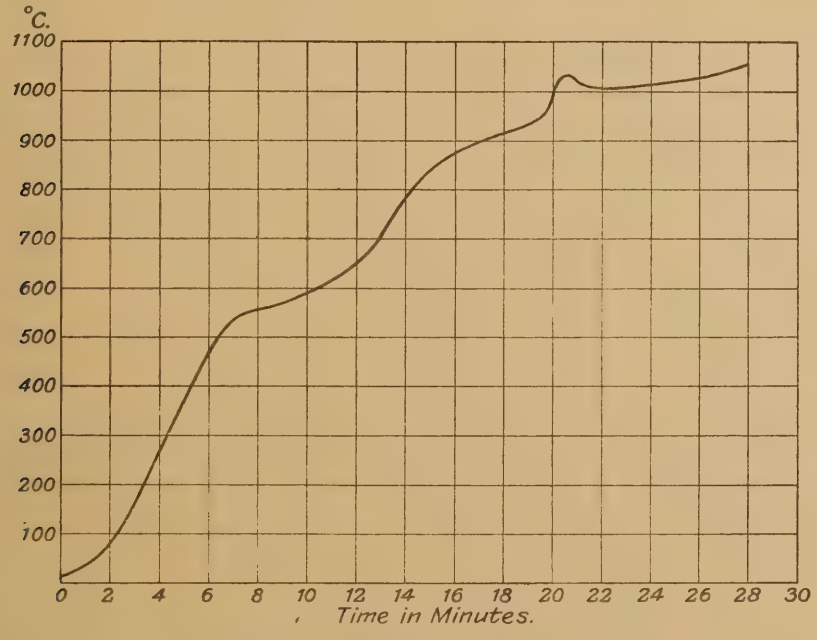


Fig. 18.—Heating Curve of China Clay.

(iii) Sillimanite appears to be formed at a higher temperature.

J. W. Mellor [3] suggests that the crystalline substance formed at 1000° C. is alumina, but this has not yet been proved. At present, the X-ray spectrum analysis of calcined china clay does not help very much as regards the elucidation of its chemical constitution.

A method which has proved useful in the case of china clay and of some fireclays consists in heating the material in an electric furnace, the temperature of which rises quite steadily, and observing the rise of temperature of the clay during a number of successive intervals of time. If an inert substance, such as firebrick dust, is heated in

[1] The fact that the percentage of water absorbed by calcined clay is considerably lower than that absorbed by a similarly calcined mixture of alumina and silica in the same proportions appears to show that the products of calcination of clay are not free silica and free alumina, but a compound containing both these oxides.

[2] *Trans. Eng. Cer. Soc.*, **22**, 106 (1922–23).

[3] *Ibid.*, p. 105.

this way, the time-temperature graph of the material is the same shape as the graph of the furnace, which should be quite regular.

If a sample of raw fireclay or china clay is examined in this manner, the time-temperature curve will be similar to that shown in fig. 18. Instead of being a simple curve, this shows a " halt " in the rise of temperature at about 200°–300° C.,[1] a second " halt " at 500°–600° C., and a sudden rise in temperature due to the material becoming hotter than the furnace at about 925° C. Mellor and Holdcroft found a further kink in the curve at 1100°–1200° C., but they consider that this is not a critical point, but is merely due to the cooling of the clay to the temperature of the furnace. P. Satoh [2] found a further exothermal reaction at 1200°–1300° C.

The first two " halts " are due to heat being absorbed by some endothermal chemical changes taking place in the clay ; the third change of temperature is due to an exothermal or heat-producing reaction which, according to Mellor and Holdcroft, is due to the commencement of the condensation or polymerisation of any free alumina present, but Knote and Ashley have independently indicated that it may possibly be due to the formation of sillimanite ($Al_2O_3SiO_2$), and W. and D. Asch consider this point to mark the polymerisation of anhydride formed at 500°–600° C.

The change at 1200°–1300° C. appears to be due to the formation of sillimanite.

The first halt (at 200°–300° C.) appears to be associated with the dehydration of colloidal matter, but this has not been fully investigated ; it is comparatively unimportant.

The second change (usually between 500°–600° C., but *in vacuo* at 300°–400° C.) coincides with the evolution of the water of constitution of the clay and clearly indicates the decomposition of the clay. The nature of this decomposition is not known ; Sokoloff, like Mellor and Holdcroft, maintains that the clay is dissociated into free alumina, free silica, and steam, but it is possible that various compounds of silica and alumina (corresponding to one or more anhydrides, $xAl_2O_3ySiO_2$, with or without free silica) may be formed.[3] That the decomposition of the clay accompanies the loss of water is shown in Table CX, due to A. M. Sokoloff.[4]

TABLE CX.—*Effect of Heat on Gluckov Kaolinite*

Temperature, ° C.	Loss of Water, per cent.	Soluble Alumina, per cent.	Molecular Ratio, $Al_2O_3H_2O$.
300	0·72	2·12	1 : 2·94
400	0·67	2·08	1 : 3·10
600	10·49	28·46	1 : 2·71
700	11·92	32·30	1 : 2·71
800	12·99	34·66	1 : 2·67

[1] This does not occur with pure china clay.

[2] *J. Amer. Cer. Soc.*, **4**, 182 (1921).

[3] Knote, *Trans. Amer. Cer. Soc.*, **12**, 226 (1910) ; W. and D. Asch, *The Silicates in Chemistry and Commerce.*

[4] *Zeit. Kryst. Min.*, **55**, 195 (1915) ; *Ber. Tech. Inst. K. Nikolaus I.*, **22**, 1 (1913).

Corresponding results with china clay, alumina, and silica, obtained by Mellor and Holdcroft, are shown in Table CXI.

TABLE CXI.—*Decomposition of Clay by Heat*

Temp.	Kaolin.			Alumina.		Silica.	
	Loss on Heating.	Soluble Matter.		Loss on Heating.	Soluble Matter.	Loss on Heating.	Soluble Matter.
		Alumina.	Silica.				
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
110	12·64	0·08	0·12	..	..	16·00	2·60
600	1·37	0·16	0·16	2·45	42·96	..	1·36
700	0·62	0·12	0·98	2·41	20·40	..	1·36
800	0·56	0·12	0·68	1·58	7·84	1·24	1·12
900	0·23	0·12	0·20	1·65	5·92	0·43	0·76
1000	0·25	0·06	0·16	0·05	..	0·05	0·68
						(at 1200° C.)	

This Table shows the increased insolubility of the alumina with a rise in temperature above 600° C. Mellor and Holdcroft suggest that this is due to some change (polymerisation ?) in the alumina. They state that alumina from different sources behaves differently, but point out that the alumina from aluminium nitrate behaves very similarly to that in china clay. On the other hand, the low solubility of the " alumina " in china clay suggests that a silica-alumina compound is formed as stated by J. M. Knote,[1] and separately by W. and D. Asch. The former suggests that clay, when decomposed by heat, forms a mono- and a tri-silicate ($Al_2O_3SiO_2$ and $Al_2O_33SiO_2$) ; he has also made the curious suggestion that when heated above 950° C. these two silicates may recombine to form a disilicate. He bases his suggestions on his discovery that raw clays and clays heated above 950° C. are not appreciably attacked by sodium carbonate and are only slightly soluble in hydrochloric acid, whilst dehydrated clays heated to temperatures below 900° C. are not appreciably affected by sodium carbonate, but are strongly attacked by hydrochloric acid.

W. and D. Asch, on the contrary, consider that no dissociation of the silica and alumina complex occurs, and that the effect of heat below 1000° C. is only to remove water and form a single anhydride. They claim that Mellor and Holdcroft's experiments do not indicate the formation of free silica and free alumina, but confirm their theory as to the formation of anhydrides without any change other than the loss of water. It is possible that two changes occur, viz. the formation of one or more anhydrides at 500° C., and the polymerisation of these at a higher temperature. The fact that calcined clay is more readily attacked by acid seems to confirm this.

[1] *Loc. cit.*, p. 350.

The anhydride suggested by W. and D. Asch has not yet been separated, but this does not disprove its existence.

The thermal curves of other alumino-silicates are interesting in comparison with those of clay. Houldsworth and Cobb [1] give the following results :—

Pyrophyllite ($Al_2O_34SiO_2H_2O$)—
- (*a*) Slight endothermal reaction at 480° C. (possibly due to clayey impurity).
- (*b*) Marked irreversible endothermal reaction between 720° and 830° C., quite distinct from those in the clay curves.

Allophane ($Al_2O_3SiO_35H_2O$)—
- (*a*) Endothermal reaction, 50°–140° C.
- (*b*) Endothermal reaction, 270°–350° C.
- (*c*) Endothermal reaction, 860°–905° C.
- (*d*) Slight exothermic reaction, 950°–970° C.

Halloysite ($H_4Al_2Si_2O_2$.Aq.)—
- (*a*) Endothermal reaction, 50°–130° C.
- (*b*) Endothermal reaction, 490°–560° C.
- (*c*) Exothermal reaction, 880°–930° C.

Cyanite ($Al_2O_3SiO_2$)—
- (*a*) Irreversible endothermic reaction, 775°–850° C.

Andalusite ($Al_2O_3SiO_2$)—
- (*a*) Very slight exothermic reaction, 940° C.

Sillimanite (India) ($Al_2O_3SiO_2$)—
- (*a*) Slight endothermal reaction, 480° C.
- (*b*) Exothermal reaction, 950° C.

} Possibly due to clay impurity.

The Synthesis of Clay

When any soluble acid is converted into a salt by the addition of an alkali or base, the acid may be liberated by treating the salt with an acid which is stronger under the conditions of the experiment. So far it has not been possible to obtain clay by the similar treatment of any minerals which could be regarded as " salts " of clay, though some investigators claim to have prepared materials which are almost identical in chemical composition, though their physical properties are not in all respects the same. Thus, W. Pukall [2] found that when common salt (sodium chloride) and clay are heated together at 950° C. a compound is formed corresponding to the formula $8Na_2O\ 6Al_2O_3\ 12SiO_2\ 12H_2O$.[3] When this is treated with a weak acid,

[1] *Trans. Eng. Cer. Soc.*, **22**, 111 (1922–23).

[2] *Berichte d. Deutsch d. Chem. Gesellsch.*, **43**, 2107 (1910); *Sprechsaal*, **43**, 440, 452 (1910); *Chem. Centralb.*, **2**, 1100 (1910).

[3] Other investigators, when examining the action of salt on fireclay in the process of " salt-glazing," have reached the conclusion that a different compound is formed. Thus, Knett regards the following equation as expressing the formation of salt glaze: $(AlFe)_2O_3SiO_2+6NaCl=$

such as carbonic acid, however, the soda is only partly removed and some silica is also withdrawn, the final residue having a composition corresponding to $2Na_2O\ 4H_2O\ 6Al_2O_3\ 10SiO_2\ 12H_2O$. With a strong acid, such as hydrochloric acid, Pukall's salt is dissolved, and when ammonia is added an acid or highly acidic salt is precipitated which contains more hydrogen and oxygen than the original clay molecule. This precipitate also differs from the original clay inasmuch as it is completely decomposed at 350° C. with the evolution of water, whereas clay is not dehydrated rapidly below a temperature of about 500° C. Pukall's precipitate has been shown by W. and D. Asch [1] to be an alumino-silicic acid similar to, but not identical with, clay.

J. H. Collins also claimed that a material identical with china clay is produced by heating felspar with water under a high pressure. The author has repeated this experiment under varying conditions, and whilst the product is undoubtedly an alumino-silicic acid it does not appear to be identical with china clay.

S. R. Scholes [2] has been granted a patent for the production of a material very similar to clay in composition and properties by fusing a mixture of felspar or other alkaline alumino-silicate with potassium carbonate, and then boiling the fused mass with water through which carbon dioxide is passed so as to remove all the soluble salts in solution. Scholes claims that this material has been used successfully for making articles similar to those produced with natural clay, but the author's tests of a material prepared by him in the prescribed manner show that it is an alumino-silicate (not an alumino-silicic acid), and, therefore, not " clay."

It is, of course, possible that the conditions under which clay can be produced are not obtainable in a chemical laboratory, either on account of the pressures or quantities of material involved being too small or the time available being insufficient.

It is sometimes suggested that an examination of some granitic rocks—especially in Cornwall—will reveal the production of china clay from felspar by a process of slow hydrolysation as a result of which the potassium in orthoclase felspar is replaced by hydrogen and the alumino-silicate converted into alumino-silicic acid (clay), the potash being removed in solution. Subterranean saline fluids may act similarly.

$(AlNa_3)_2O_3SiO_2+Fe_2Cl_6$. The ferric chloride is further decomposed by steam, forming red ferric oxide, which dissolves in the glaze and colours the latter brown.

$$Fe_2Cl_6+H_2O=Fe_2O_3+6HCl.$$

F. H. Clews and H. V. Thompson (*J. Chem. Soc.*, **121**, 1442 (1922)) disregard the alumina, as they found the following reactions to occur between salt and silica under various conditions at temperatures between 569° and 1045° C. :—

$$(a)\ 4x\mathrm{NaCl}+y\mathrm{SiO_2}+x\mathrm{O_2}\ =2x\mathrm{Na_2O}\ y\mathrm{SiO_2}+2x\mathrm{Cl_2}$$
$$(b)\ 2x\mathrm{NaCl}+y\mathrm{SiO_2}+x\mathrm{H_2O}=x\mathrm{Na_2O}\ y\mathrm{SiO_2}+2x\mathrm{HCl}.$$
$$(c)\ 4\mathrm{HCl}+\mathrm{O_2}=2\mathrm{H_2O}+2\mathrm{O_2}.$$

In the absence of moisture only action (*a*) occurs, but in moist air all three occur, (*b*) predominating, and the reactions occurring most rapidly at 1000° C. For other formulæ, see p. 391.

[1] *Loc. cit.*, p. 346.

[2] *Eng. Pat.*, 117, 755.

According to Fiebelhorn, their action may be represented by—

$$K_2O\ Al_2O_3\ 6SiO_2 + 2H_2O = Al_2O_3\ 2SiO_2\ 2H_2O + K_2O\ 4SiO_2$$

Felspar Water Clay Potassium silicate.

Other investigators consider that the potassium silicate formed has the formula $K_2O\ 3SiO_2$, and that the one molecule of silica in the free state is either carried away with the water or remains mixed with the clay. Van Hise considers that a more correct equation is one involving the use of carbon dioxide—

$$2KAlSi_3O_5 + 2H_2O + CO_2 = H_4Al_2Si_2O_9 + 4SiO_2 + K_2CO_3.$$

Unfortunately, there is no evidence that clay is produced solely from orthoclase; on the contrary, it may be formed, as suggested by Van Hise, from andalusite, anorthoclase, cyanite, epidote, leucite, microcline, nephelite, orthoclase, plagioclase, scapolite, sillimanite, sodalite, topaz, zoisite, or garnet, or, as suggested by Rosler, by the decomposition of hauyne or analcite, or, as claimed by A. B. Jameson, from rhyolite, pumice, and various natural glasses. Under these circumstances, it is not surprising that the precise chemical constitution of clay is still uncertain.

The Chemical Constitution of Glazes

The chemical constitution of glazes and glasses is extremely complicated, and, like that of clay, is not yet properly understood. Glazes and glasses consist of substances which are amorphous and, when molten, form homogeneous fluids. When cooled under suitable conditions they do not crystallise, but retain many of the properties of a fluid of exceedingly high viscosity. When heated to a temperature much below their melting-point they become plastic and mobile, but regain their rigidity on cooling. They may, in short, be regarded as "under-cooled liquids" or "solid solutions."

Two distinct views are held as to the chemical constitution of glasses and glazes, viz.:

(*a*) That they are solid solutions of various silicates mixed together indiscriminately and not in definite proportions.

(*b*) That they are definite chemical compounds.

In the first conception of their constitution they are regarded as similar to any other mixtures of liquids, the physical properties of which must be confined within wide limits of composition as distinct from definite chemical compounds, the composition of which cannot vary. This view of their constitution seems all the more probable when it is remembered that the composition of many glasses may vary within wide limits without their physical properties being impaired. On the contrary, this permissible variation makes their use possible under comparatively rough conditions.

The view that a glass or glaze is a homogeneous mixture of several substances forming a solid solution does not exclude the possibility of its containing a large

percentage of one constituent which may be a complex chemical compound. It is well known that many definite organic compounds which are not quite pure will only crystallise with difficulty, and in some of these cases the proportion of impurity which prevents crystallisation is very small. A similar characteristic may explain why glasses and glazes possess their valuable property of remaining amorphous when solid. This analogy seems all the more reasonable when it is remembered that most glasses and glazes will crystallise if kept for a sufficiently long time at a suitable temperature, and that, on slightly altering the composition of some glasses and glazes, crystallisation readily occurs. As a general rule, the more closely the composition of a glass or glaze corresponds to that of a definite silicate, the more readily will it crystallise. On the other hand, a glass or glaze which crystallises too easily may be improved by adding rather more of one of the constituents (usually, but not always, silica) so as to remove its composition somewhat from that of a definite chemical compound.

The nature of the definite chemical compounds in glasses and glazes is not definitely known ; investigations which have been made to ascertain what eutectics are present have not been wholly successful. They may be compared to metallic alloys, but the latter appear to be composed of much simpler compounds and often contain a larger proportion of metal in the elementary state, whereas glasses and glazes appear to consist of highly complex compounds.

The chemical composition of most glasses and glazes does not correspond exactly to that of definite chemical compounds when the ordinary methods of formulation are employed. If they are assumed to have a very high molecular weight, however, it is much easier to regard them as definite compounds containing an excess of one or more ingredients, just as many commercial materials contain a variable percentage of other substances as " impurities." For instance, no one would regard a silica brick as a solid solution ; it would be considered to be composed of somewhat impure quartz—a definite chemical compound.

As the vitrified nature of glasses and glazes is one of their most valuable properties, it is generally useless to adjust their composition so that each consists of one definite chemical compound ; such a product would seldom be satisfactory, as it would have a great tendency to devitrify or crystallise, and so spoil the transparency and uniformity of the glass or glaze and prevent its being used for its intended purposes. When a matte or crystalline glaze is required, however, the glaze should approach more nearly in composition to a single definite compound in order to facilitate the production of a mass of minute crystals and so produce the required decorative effect.

Many coloured glazes owe their colour to the formation of definite chemical compounds. Thus, some blue glazes are due to the formation of copper and cobalt zeolites (see also p. 395).

The Chemical Constitution of Magnesia

Magnesium oxide—like silica—occurs in several allotropic forms which may be due to the different number of atoms in the molecules of the various substances. Usually the oxide is expressed by the formula MgO, though it is probable that the

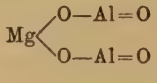
true formula is a multiple of this, and that further heating causes a modification (such as polymerisation) in the complexity of the molecule. The two most important allotropic forms are readily distinguished, as shown by J. W. Mellor, by their specific gravity, and the conversion of one form to another is shown by the change in the specific gravity. If the light-burned magnesia be described as the α-form, then the β-form—which is identical with periclase—may be formed by heating the α-form to 1300° C.

Although both forms have the same chemical composition they differ in several important respects. Thus, the α-variety is soluble in acids, whilst the β-variety is very resistant to their action. The β-form (periclase) is crystalline, whilst the α-form is amorphous. The former is the more desirable as a refractory material on account of its constancy of volume at different temperatures. Although the conversion commences at about 1300° C., it is necessary to attain a higher temperature, 1530°–1790° C., if the rate of conversion is to be reasonably rapid. The best method of effecting this conversion is to heat the magnesia in an electric furnace. N. Parravano and C. Mazzetti [1] state that the change commences at 800° C., but proceeds very slowly at this temperature. This figure agrees closely with the results obtained by Ditte [2] in his measurements of the density of the oxide after it has been heated at different temperatures. Other inversion temperatures suggested include Le Chatelier's [3] figure of 1600° C., and that of Campbell, who gives 1100° C. as the temperature of transformation.

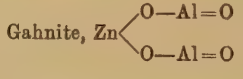
The difference in chemical constitution between the α- and β-forms of magnesia has never been determined. It is probably analogous to the difference between charcoal and diamond.

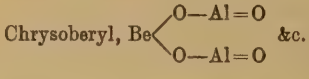
The Chemical Constitution of Spinels

Spinels are compounds of aluminium, oxygen, and various metals, in which the two former constituents play the part of an acid radicle, so that spinels may be regarded as *aluminates*. The simplest contain only one metal besides the aluminium, whilst others are more complex and have three or more metals. The mineral spinel is a magnesium aluminate having, according to Mellor, the following formula :—



Other minerals belonging to the spinel class include





They are characterised by a high degree of refractoriness, and some of them form brilliant gem stones.

[1] *Annali Chim. Appl.*, **7**, 3–12 (1923).
[2] *Comptes Rend.*, **73**, 111, 191, 270 (1871); **76**, 108 (1873).
[3] *Le Chauffage*, 339 (1912).

The Constitution of Silicon Carbides and Oxycarbides

Various substances—chiefly known by their trade names—are commonly regarded as silicon carbide, the typical formula for which is SiC. Of these materials carborundum and crystolon are true silicon carbides, silundum and siloxicon are carboxides, whilst the chemical nature of silfrax, silit, and some other materials made from carbon and silica are not clearly understood. It is probable that they are mixtures of carbides and carboxides in indefinite proportions, and, in some cases, they also appear to contain some silicon nitride.

Silundum and siloxicon appear to be best represented by formulæ between Si_2C_2O and Si_7C_2O, or multiples of these.

The arrangement of the atoms forming these carbides and allied materials has not yet been satisfactorily determined, but some information is given on p. 324.

The Chemical Constitution of Lime

Lime occurs in two forms, amorphous and crystalline, the crystalline variety being formed when amorphous lime is heated at a high temperature for a long time. The crystalline variety occurs in two allotropic forms, the inversion point being at about 420° C.

The Chemical Constitution of Iron Oxides and Hydroxides

Iron oxides occur in three forms: ferrous oxide (FeO), ferric oxide (Fe_2O_3), and magnetic oxide (Fe_3O_4). R. B. Sosman and J. C. Hostetter [1] consider that there is a continuous series of mixed crystals containing iron and oxygen varying in composition from about Fe_3O_4 at one end to Fe_2O_3 at the other. The magnetic permeability diminishes as the oxygen content increases. The decomposition-pressure also rises with increased oxygen-content. As the centre of the curve representing this is nearly horizontal, A. Smits and J. M. Bijvoet [2] suggest that there may be two series of mixed crystals, and that the centre of the curve represents a mechanical mixture of both these series. Other investigators regard the various mixtures obtained as solid solutions of magnetic oxide in ferric oxide or *vice versa*.

Sosman states that ferric oxide dissociates on heating, forming free oxygen and a solid solution of magnetic oxide in ferric oxide, the dissociation pressure falling as the percentage of FeO in the solid increases until the dissociation pressure of Fe_3O_4 is reached, when the latter dissociates into oxygen and a mixture of oxides whose character has not yet been determined. Ferric oxide appears to have an inversion point at 678° C., which is sharp and reversible and affects its magnetic susceptibility, whilst another change, according to Honda, occurs at –40° C. Magnetic oxide is also said to have an inversion point at about 530° C., when its magnetic properties also change.

[1] *J. Amer. Chem. Soc.*, **38**, 807 (1916); *Trans. Amer. Inst. Min. Eng.*, **58**, 409, 439 (1917).
[2] *Proc. Amst. Acad.*, **21**, 389 (1919).

The chemical constitution of the iron hydroxides is largely uncertain. Limonite —a ferric hydroxide to which is usually given the formula $Fe_2(OH)_6$—appears to be very variable in composition, and there are good reasons for supposing that in the iron hydroxides much of the " water " present is in the form of " colloidal water " (p. 336) and not as true " water of constitution." If that is the case, the various colours of these different hydroxides are really due to the colloidal matter present and not to the existence of innumerable ferric hydroxides as is sometimes supposed.

The Chemical Constitution of other Refractory Materials

Comparatively little work has been done on the constitution of the more unusual refractory materials. There are many evidences, however, which show that their constitution is by no means simple. Thus, **chromite** shrinks considerably at about 500° C., probably on account of polymerisation. **Zirconia** appears to polymerise similarly to magnesia, and **carbon** has a very complex allotropy, graphite being the stable form at temperatures above 500° C.

According to G. Asahara,[1] amorphous carbon, when examined by X-rays, shows interference rings, but no distinct maxima ; the absence of the latter may be due to distributed intensity. Carbons produced by the decomposition of gases, such as carbon monoxide, acetylene, or carbon disulphide, or from Fe_3C and coal, also show interference figures, thus indicating that " amorphous " carbon is really composed of extremely minute crystals.

W. H. Bragg [2] considers the difference between diamond, graphite, and other forms of carbon to lie in the bonding of the layers of electrons. Thus, he considers that, as in a diamond, the carbon atom lacks four electrons to complete its second layer, it shares these in common with each of four of its neighbours. He regards the layers of atoms in graphite as being joined by weak forces, though the atoms in each layer are united as firmly as in the diamond. He suggests that in organic crystals there is no sharing of electrons and no electrical separation into ions, one molecule being attached to the next in a very weak manner.

The constitution of the complex mixtures, solid solutions, etc., which occur in the various raw materials and final products in the ceramic industries, cannot be dealt with in this section, as the varieties are far too numerous. In Chapter XI, however, the various reactions which may take place under different conditions are described, from which the constitution of any particular mixture may be predicted approximately, though the reactions are so complex, and our knowledge is at present so incomplete, that no definite rules can be laid down with respect to many of the changes which may occur.

[1] *Sci. Papers Inst. Phys. Chem. Research*, **1**, 23–9 (1922) ; *Jap. J. Chem.*, **1**, 35–41 (1922).
[2] *Min. Mag.*, **19**, 316–8 (1922).

CHAPTER IX

THE CHEMICAL COMPONENTS OF CLAY AND CERAMIC MATERIALS AND PRODUCTS

The chemical constitution of " pure clay " is largely a matter of academic interest, though, when greater knowledge concerning it is available, it will probably be of great practical value in extending the uses for which clay may be employed, and in improving the quality of articles and materials made from clay.

Chemically pure clay is almost a scientific curiosity, but more crude and impure clays and other ceramic materials are of such great commercial importance, that a knowledge of their other constituents is essential if progress is to be made in the ceramic industries.

The presence and amount of the components or constituents of clays and allied materials are ascertained by chemical analysis, so that this subject may conveniently be considered prior to dealing with the individual components.

Chemical Analysis.—The results of a chemical analysis of any mineral substance are usually expressed in terms of various oxides, such as silica, alumina, ferric oxide, titanic oxide, lime, magnesia, soda, potash, carbon dioxide, sulphur trioxide, etc. Elements such as chlorine, which are not found in combination with oxygen in most minerals, are expressed as elements, and, if necessary, a correction must be made for any oxygen reported as combined with sodium (in the form of soda) when in reality some or all of the sodium is present as sodium chloride.

Another matter which requires special attention is the custom of reporting the iron present as ferric oxide (Fe_2O_3). This is incorrect, as iron only occurs very infrequently in this form in clays. Its usual form of occurrence is in the ferrous state, as pyrites or marcasite, and to a small extent in the ferric state as limonite. It is often preferable to report the iron as ferric oxide and ferrous oxide, and a determination of the amount of ferric sulphide present is of value in some cases. As 160 parts of ferric oxide correspond to 120 parts of ferric sulphide and to 144 parts of ferrous oxide, the actual difference in the percentage of each of these substances, when any or all of them are converted into ferric oxide and weighed in this form, is not often serious, but, where the matter is important, a correction must be made.

A similar correction may sometimes have to be made for other substances.

A chemical analysis, as usually made, does not indicate in any way how the various elements (or oxides) are combined, but merely gives the total amount of

each. Hence, when it is desired to know what substances are present, special methods of analysis must be employed.

It is possible to assume that certain elements will combine together in certain ways, and thus to obtain a very fair idea of the probable components of a mixture, but unless such assumptions are exceptionally well founded, they may lead to serious error.

The chief value of a chemical analysis is to be found in the information it provides as to the proportion of each element (or oxide) present. From this information, any predictions may be in the nature of fairly safe guesses or they may be little better than speculations. Thus, if a chemical analysis shows that a clay contains a high proportion of fluxes, such as lime, soda, or potash, it will usually be safe to assume that the clay will not be highly refractory. It would not usually be safe to predict, as is sometimes done, the temperature at which the material would fuse or vitrify, as this will depend largely on the nature of the chemical compounds present. Thus, soda and potash, in the form of mica, are more detrimental to the refractoriness of a clay than when they are in the form of felspar, as the former fuses more readily than the latter, and soda, in the form of sodium silicate, is still more readily fusible.

A chemical analysis is also valuable in showing the presence of some deleterious ingredients, such as (i) lime, which may destroy bricks and tiles made of clay containing it; or (ii) ferric oxide, which may either discolour a clay or enhance the beauty of the product, according as a white or red material is desired.

Very great care is needed in drawing conclusions from the results of a chemical analysis, as a high proportion of calcium carbonate is a valuable constituent in some "clays," because of its bleaching and vitrifying power, but in clays used for other purposes its presence may be highly objectionable.

It should scarcely need to be pointed out that unless an analysis is complete its value may be very small as the omission of a small percentage of some constituents may make an adequate interpretation of the results of the analysis very difficult. For this reason, no constituents should be estimated "by difference" in order to make the analysis appear to be complete, though this is frequently done. It is especially important that the alkalies should not be estimated "by difference," as a small error in the proportion of them may have an important effect on the properties of the material. It is sometimes tempting to do this, as the work required to determine the alkalies is as great as that of determining all the other constituents put together.

Space does not permit a detailed description of the methods employed in the ultimate chemical analysis of ceramic materials, and the reader who desires information in this direction should refer to other volumes dealing more particularly with this subject, especially Mellor's *Quantitative Inorganic Analysis* (Griffin, London).

Sampling.—It is obviously essential that a chemical analysis, to be of value, must be truly representative of the material with which it deals. If it relates to a large mass of material, the analysis must be typical of the whole and not of one abnormal portion. Yet, unless special care is taken in procuring the sample to be analysed, such a typical product or "fair average sample" will not be obtained. A single

lump selected haphazard from the mass will be most unlikely to be fairly representative, and even a large number of such casually selected samples may not be satisfactory. Very frequently large variations occur, so that it is most important that proper care should be taken to obtain a truly representative sample. Failure to do this may result in heavy financial loss. When a large, natural deposit of clay or other material is to be analysed, the samples should be taken from many different parts of the bed, both horizontally and vertically. It is often desirable to have several distinct analyses made of different parts of the deposit, so as to determine whether the material is constant in composition throughout the whole bed. Where the material appears to be fairly uniform, about 1 per cent. of the whole of the material may suffice for the preliminary material from which the final sample is to be taken, but with a very heterogeneous material, 2 or even 5 per cent. may be necessary to obtain a reasonably typical sample. The preliminary sample should be composed of numerous smaller samples selected systematically from every part of the deposit and not merely from those which are the most readily accessible. When obtained, this preliminary sample should be treated as described later.

If the material to be examined is contained in trucks or in a heap, it is equally necessary to take an ample quantity in the form of small samples to produce a large preliminary sample, though sometimes the whole mass is treated as a preliminary sample. Samples from large quantities of material contained in trucks or shiploads are often taken by means of mechanical appliances.

The *preliminary sample* obtained as just described is next treated as an original material from which a representative sample is to be obtained by the process known as " quartering," which is usually effected as follows :—

The material should be thoroughly mixed and placed in a symmetrical and rather flat pile and divided into four equal parts. One of these parts is removed, the material in it is again mixed and then quartered, this being continued until a sample weighing about 28 lb. is obtained. This is coarsely crushed and again quartered, one quarter (about 7 lb.) being sent to the analyst, who should then obtain a representative sample by still further crushing and quartering until a suitable quantity is obtained. When very small samples are required for analysis, fine grinding and thorough mixing are very essential.

The samples sent to the analyst should not be ground too finely before transit, or any oxidisable compounds present may be oxidised and so render the results inaccurate. Thus, ferrous oxide may be oxidised to ferric oxide. It is also desirable to avoid, as far as possible, the use of iron or steel instruments in sampling, grinding, and sifting, so as not to include any adventitious iron in the sample. Sieves made of phosphor-bronze may be used instead of iron or steel ones for the same reason.

CHEMICAL COMPONENTS OF CLAYS AND CLAY PRODUCTS

Commercial clays consist primarily of one or more alumino-silicic acids, as described on p. 344, together with a varying proportion of other substances which are commonly termed " impurities."

As most of the " impurities " in ceramic materials reduce their resistance to heat they are often termed *fluxes*, though their ability to effect the fusion of the material depends largely on circumstances, and at low temperatures they have no fluxing action at all.

The nature of the alumino-silicic acids has already been dealt with in Chapter VIII and need not be further considered. Attention may, therefore, be concentrated in this section on other materials present in clays, and their effect on the behaviour of the clay under different conditions. Although any component of a clay other than the alumino-silicic acid may be regarded as an " impurity," the fact must not be overlooked that many clays owe their technical importance to the presence of some " impurities." For instance, the pleasing red colour of some terra-cotta, the imperviousness and resistance to corrosion of stoneware, the delicate translucency of china-ware, and the enormous resistance to crushing of some engineering bricks, are all due to the presence of a suitable proportion of certain " impurities " which impart to these materials their valuable characteristics.

A pure alumino-silicic acid may be highly refractory, but it will usually be very weak when burned, owing to the absence of " impurities " in the form of bases with which to form a vitrifiable bond which will unite the clay particles into a mass of great strength.

The proportion of impurities allowable in a clay will, of course, depend on the purpose for which it is to be used. Thus, where it is to be employed in the manufacture of whiteware, the clay must not, of course, contain a large proportion of colouring impurities, such as iron oxides, etc. Similarly, where a clay is to be used as a refractory material it must be as free as possible from fluxes, as these would reduce its resistance to heat. As a chemical analysis does not reveal the state in which the various substances are combined, it is very important, in analysis of clays, silica rocks, and other materials containing alumino-silicates, to remember that the proportion of fluxes shown by such analysis does not represent the total amount of impurity present, as the silica and alumina with which the fluxes are combined (or with which they will combine when the material is heated) will be included in the total amounts of silica and alumina, so that the presence of 1·6 per cent. of potash may represent 10·0 per cent. of impurity in the form of felspar, the 1·8 per cent. of alumina and the 6·6 per cent. of silica being included in the total silica and alumina present. Hence, a clay which may appear to contain a very small percentage of lime, magnesia, potash, and soda may actually contain 20 per cent. of minerals other than clay. For this reason it is often more important to know the mineralogical composition of a clay or other ceramic material than its composition as shown by chemical analysis (see Chapter X).

As the percentage of *moisture* and *loss on ignition* are very variable in most ceramic materials, it is often convenient to calculate the analysis on the dried or burned material if a large number of comparisons is to be made. Such a calculation may involve small errors as the nature of this material removed by drying or burning may not be exactly known ; these errors are negligible in most cases, though occasionally they are important.

Impurities in Clays

The effect of impurities in a clay depend upon :

(*a*) Their nature.
(*b*) The proportion in which they occur.
(*c*) The size and shape of the grains of clay and of the impurities.
(*d*) The conditions under which interaction takes place, including (i) the temperature reached, (ii) the duration of the heating, (iii) the atmosphere of the furnace or kiln, and (iv) the effect of any other substances which may be present.

The principal impurities in clays may be classed as follows : (*a*) silica, (*b*) alumina, (*c*) alkaline silicates and alumino-silicates, (*d*) iron compounds, (*e*) calcium compounds, (*f*) barium compounds, (*g*) magnesium compounds, (*h*) titanium compounds, (*i*) manganese and other compounds which occur in very small proportions in some clays, (*j*) moisture and colloidal water, (*k*) carbonaceous matter and combined water (*i.e.* water of constitution and of crystallisation).

Various other impurities which may occur in certain clays are usually of minor importance.

Silica occurs in clays and allied minerals (*a*) in the *free* state, as quartz or other form of crystalline silica and as amorphous, hydrated, or colloidal silica, and (*b*) *in combination* (i) with alumina in the form of clay and other alumino-silicic acids, or with fluxes and alumina in the form of felspar, mica, or other alumino-silicates, or (ii) with various bases forming soluble silicates, such as wollastonite ($CaOSiO_2$), etc.

The effects of free silica in clay are as follows :—

1. It reduces the plasticity (p. 270).
2. It lessens the shrinkage on drying (p. 96) and firing (Chapter XIII).
3. It reduces the tensile and crushing strengths (p. 151).
4. It may increase the resistance to sudden changes in temperature (see Chapter XIII).
5. It reduces the refractoriness in many cases, though not in all (see also Chapter XIII).

Combined silica does not affect the melting-point in the same way as free silica.

The size of the grains is also important, as very small particles of silica will often act on a flux under conditions where larger particles of silica increase the refractoriness of the mass. In some cases silica will increase the refractoriness of a clay, quite apart from the size of the particles, especially if the " clay " is very impure ; any improvement which may be effected in this manner by the addition of silica is of very limited extent. Seger found that, with pure clay and pure silica, the melting-point is lowered, with an increase in the proportion of silica until a molecular ratio corresponding to $Al_2O_3 : 17SiO_2$ is reached, after which further additions of silica raise the melting-point. Sieurin and Carlsson [1] found that silica reduced the

[1] *Loc. cit.*, p. 149.

refractoriness of a clay when under load, the minimum resistance being reached with a mixture containing 60–70 per cent. of silica. Fig. 38, due to Seger, shows the refractoriness of mixtures of pure silica and alumina. If a clay contains more than two molecules of silica to each molecule of alumina, and also a high proportion of fluxes, it will usually have a low refractoriness; Bleininger and Brown have also suggested that no clay should be used for refractory purposes which contain more than 0·225 molecules of fluxes or 2 molecules of silica to each molecule of alumina. The effect of silica on the refractoriness of a clay is also clearly shown by Ludwig's chart (p. 382).

Alumina occurs in clays in the form of felspars, mica, hornblende, tourmaline, and other similar alumino-silicates, all of which are moderately fusible. Free alumina is seldom found in clays, but is abundant in bauxites and laterites, and is therefore present in some clays derived from these materials. Aluminous compounds, apart from the clay, have the following effects on clays if the temperature is sufficiently high :—

1. They reduce the plasticity of the clay, as they are non-plastic (p. 270).
2. They increase the strength of the fired clay (p. 147).
3. They increase the density and impermeability of the burned ware (p. 66).
4. They reduce the refractoriness of the clay if they are in the form of alumino-silicates, but free alumina increases the refractoriness of most clays (*below*).

Sieurin and Carlsson [1] found that alumina up to 70 per cent. increases the refractoriness under load (p. 149). With 70–80 per cent. of alumina, however, the refractoriness suddenly falls, but increases slowly with still higher percentages.

L. Bertrand [2] found that raw clays containing more than 29 per cent. of alumina, or fired clays containing more that 32 per cent., had softening points over 1650° C. Those containing 20–29 per cent. of alumina in the raw clay, or 21–32 per cent. in the fired material, had softening points often above but sometimes lower than 1650° C. Clays with less than 20 per cent. of alumina (or 21·5 per cent. with the fired material) generally soften at temperatures below 1650° C., though occasionally such clays are found which soften above this temperature.

Alkaline Silicates and Alumino-silicates.—The chief alkalies in clay occur—

(i) Silicates and alumino-silicates (incl. felspar and mica) being so typical it is often assumed that all other insoluble alkali compounds in clays behave like either felspar or mica, though others may also occur. The effect of felspar and mica on the refractoriness of clay is shown in figs. 19 and 20, due to Simonis and Rieke respectively.

(ii) As soluble salts, such as potassium sulphate, sodium sulphate, and sodium chloride. These salts also reduce the refractoriness of the material; they may also, if present in sufficiently large proportion, form a white scum on the surface of the articles either before or after firing. Soluble salts also affect the plasticity of clay (p. 272), some tending to increase it, though most of them reduce it. According to Dorfner, in stoneware, porcelain, and other vitrified ware, the higher the molecular

[1] *Loc. cit.*, p. 149.
[2] *La Céramique*, **25**, 153–157 (1922).

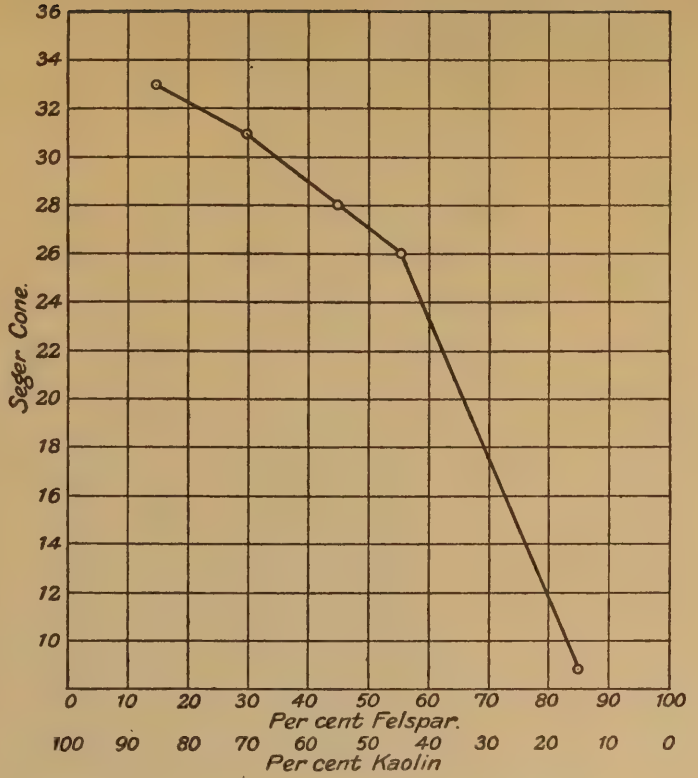


FIG. 19.—FUSION CURVE OF FELSPAR-KAOLIN MIXTURES.

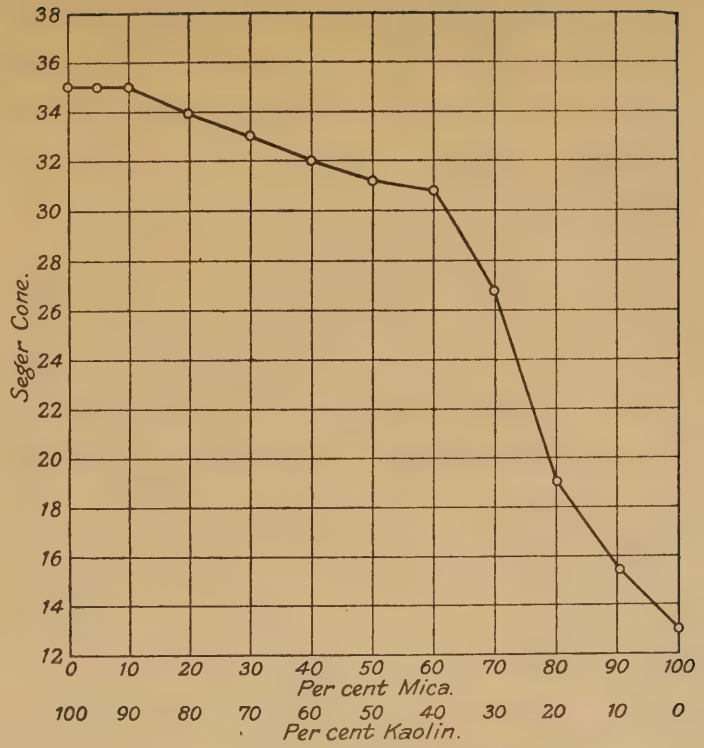


FIG. 20.—FUSION CURVE OF MICA-KAOLIN MIXTURES.

proportion of potash, the more fusible is the mass, whilst the higher it is in lime the less fusible it becomes. On the other hand, the lower the proportion of potash, the more plastic will be the material. In incompletely sintered ware, such as faience and earthenware, the larger the proportion of potash, the more solid will be the body with a given firing temperature.

Iron Compounds.—The various iron compounds which may occur in clays have been mentioned on p. 97. As regards their chemical effect, they may be classed as (*a*) ferric oxide (Fe_2O_3), (*b*) ferrous oxide (FeO), (*c*) magnetic iron oxide (Fe_3O_4), (*d*) iron sulphides (FeS and FeS_2), (*e*) iron carbonates ($FeCO_3$), (*f*) ferrous and ferric hydroxides which behave like the respective oxides, (*g*) ferro-silicates and ferro-alumino-silicates, (*h*) soluble iron salts (chiefly ferrous sulphate).

The chief effects of iron compounds in clays are :

(i) They effect an alteration in the colour (see Chapter II).
(ii) They may reduce the refractoriness of the clay.
(iii) Soluble iron compounds may form a scum on the ware.

A very small quantity of iron oxide is undesirable where white ware is required, unless a comparatively large proportion of calcium carbonate in the clay is not objectionable, when a correspondingly large proportion of iron may be present, as its colour will then be neutralised on heating, and a white product formed instead of the usual red colour due to ferric oxide (see also p. 102).

Ferric oxide does not greatly reduce the refractoriness of a burned clay, provided it is always maintained in an oxidising atmosphere, as ferric oxide is highly refractory. In a reducing atmosphere, on the contrary, it acts as a powerful flux. Sieurin and Carlsson [1] found that when a clay containing ferric oxide is heated under pressure the iron oxide reduced the refractoriness rapidly if less than 6 per cent. were present, slightly if between 6 and 12 per cent. were present, and rapidly if more than 12 per cent. of iron oxide were present.

Magnetic and ferrous oxides are very undesirable, as they are powerful fluxes, and combine with clay to form mobile, fusible silicates, ferro-silicates, and alumino-silicates, the most fusible silicate being fayalite (melting-point, 1050–1075° C.) and the most fusible alumino-silicate, according to Rieke, corresponding to the formula $2Fe_2OAl_2O_32SiO_2$, which melts at Cone 3a (1140° C.).

Ferrous carbonate, when present in a clay, may either be reduced in the burning process to ferrous oxide with the evolution of carbon dioxide (the oxide then acts as a flux, and produces black, slaggy masses of fusible silicates which are very undesirable), or it may be oxidised to ferric oxide, and be comparatively harmless unless white ware is required.

Ferric sulphide (pyrites), when heated, loses half its sulphur at 400°–600° C. and the rest at a higher temperature. In a reducing atmosphere it produces ferrous oxide which acts as a powerful flux, but if the burning is carried out entirely in an oxidising atmosphere, the iron may be completely oxidised to form ferric oxide, which does not greatly affect the refractoriness of the clay.

[1] *Loc. cit.*, p. 149.

Ferro-silicates and ferro-alumino-silicates behave in a manner similar to felspar, *i.e.* they are moderately fusible and increase the amount of vitrified matter or " bond " in the fired ware and so slightly increase the strength of the ware. According to their colour they may improve or spoil the appearance of the ware. Some ferro-silicates, such as nontronite (p. 97), appear to be decomposed into their constituent oxides when heated.

Soluble iron compounds usually produce a light-coloured scum on the surface of the dried ware containing them. On burning, this is usually converted into unpleasant brown or black patches.

Calcium compounds occur in clays as (*a*) *calcium carbonate*, in the form of crystals of calcite or aragonite, or as chalk or other form of limestone. Occasionally it occurs in the form of fragments of shells; (*b*) *calcium sulphate*, in the form of gypsum and selenite; (*c*) *calcium phosphate*, in the form of coprolites and other fossilised animal excreta; (*d*) *lime felspars*, chiefly oligoclase and anorthite; and (*e*) other calcium silicates and alumino-silicates.

When calcium carbonate or calcium sulphate is heated, it evolves carbon dioxide or sulphur trioxide, and forms lime, which is a powerful flux and readily combines with silica and with alumino-silicates to form a mobile fluid of great corrosive power. When cooled, this fluid solidifies to a glassy mass, which forms a strong bond and produces impervious and acid-resisting ware.

Calcium phosphate, when heated to redness, exchanges phosphorus pentoxide for silica, and forms a calcium silicate having the same properties as that produced by the action of lime.

Calcium silicates and other stable calcium compounds melt at a comparatively low temperature, and then act as fluxes in a manner similar to lime, but much more slowly. The calcium alumino-silicates produce a tougher and more viscous bond than the simple silicates, and are, therefore, preferable. The lime produced by heating some calcium compounds (as explained above), if present in an amount equivalent to less than 10 per cent. of lime, reduces the refractoriness of kaolin from Cone 35 (1770° C.) to Cone 15 (1435° C.), but if 10–20 per cent. of lime is present the refractoriness increases to Cone 19 (1520° C.) and then falls with 34·5 per cent. of lime to Cone 7 (1230° C.). With 50 per cent. of lime the refractoriness rises again to Cone 19 (1520° C.), but with 59·7 per cent. of lime it falls to Cone 13 (1380° C.), after which, with 70 per cent. of lime, it rises sharply to Cone 27 (1610° C.). Fig. 34 shows the phase diagram of the lime-silica system according to Day and Shepherd.

Clays containing a larger proportion of silica than is present in kaolin (*i.e.* more than two molecules of silica to each molecule of alumina) are more rapidly reduced in refractoriness by small amounts of lime than those of a composition similar to kaolin. Thus, according to Rieke, the addition of 7·6 per cent. of lime reduces the refractoriness of a mixture corresponding to $Al_2O_3 4SiO_2$ to Cone 12 (1350° C.), whilst mixtures corresponding to $Al_2O_3 2SiO_2$ or to $Al_2O_3 3SiO_2$, with about 6 per cent. of lime respectively, fuse at about Cone 28 (1630° C.). The addition of about 20–40 per cent. of lime reduces the refractoriness of a mixture corresponding to $Al_2O_3 4SiO_2$ to below Cone 6 (1200° C.), but the addition of 62 per cent. of lime to such mixture increases its

refractoriness to about Cone 26 (1580° C.). Mixtures corresponding to $Al_2O_3 3SiO_2$ are the most fusible when about 48 per cent. of lime is added to them. The slag produced by the combination of lime with silica and other minerals is very mobile when fused, and, consequently, a mass containing it loses shape very shortly after the lime compound begins to fuse.

According to Pukall, a high proportion of lime in a clay causes fritting and fusion rather more slowly than an equally high proportion of potash. Thus, with same total molecular ratio of bases (RO) to alumina and silica, a high molecular proportion of potash will form a stoneware at Cone 7 (1230° C.), whilst a high molecular proportion of lime will produce a good earthenware, except where the proportions of silica or alumina are also high. At very high temperatures, both these mixtures will produce porcelains unless the alumina or silica is excessively high.

According to Dorfner, the higher the molecular proportion of lime in the bases, the total RO being constant, the less fusible is the product if a porcelain, stoneware, or other vitrified ware is being produced; but in a porous ware, the higher the molecular proportion of lime in relation to the total bases (RO), the more friable will be the ware and the less the liability of the glaze to craze.

Barium compounds do not occur to any great extent in clay, but when present they act in a manner similar to the corresponding lime compounds.

Magnesium compounds occur in clay chiefly as magnesite ($MgCO_3$) and as complex silicates and alumino-silicates. They act as fluxes and reduce the refractoriness of clays in which they occur, though they are less powerful than the corresponding lime compounds and act more slowly, so that they are usually less harmful and less likely to cause the ware to lose its shape when heated.

The slag produced by the action of magnesium compounds on clay is also more viscous, thus further preventing the occurrence of a rapid loss of shape.

Rieke has found that magnesite gradually reduces the refractoriness of kaolin from Cone 34 (1750° C.), with less than 1 per cent. of magnesite, to Cone 10 (1300° C.) with 40 per cent. of magnesite. With more than 45 per cent. of magnesite the refractoriness is increased, and with 64 per cent. the refractoriness of the mixture is the same as that of Cone 29 (1650° C.). When an excess of silica is present, the refractoriness is reduced more rapidly, 30 per cent. of magnesite sufficing to reduce the refractoriness of a mixture containing 133·3 parts of free silica to 100 parts of kaolin to Cone 10–11 (1300–1320° C.).

Titanium compounds act as fluxes in clay, but, as they usually occur in only small proportions—seldom exceeding 2 per cent.—their effect is frequently negligible.

The presence of 10 per cent. of titanic oxide in silica reduces the refractoriness of the latter from Cone 36 to Cone 33–34; the eutectic (which melts at Cone 20) contains 40 per cent. of titanic oxide. Titanic oxide has a similar effect on alumina, 20 per cent. of it reducing the refractoriness of alumina from Cone 42 to Cone 37; larger proportions are progressively more active.

Manganese compounds when present in clays and clay products act as fluxes, and in many respects resemble the corresponding ferrous compounds. Rieke has found that the addition of 7·38 per cent. of manganese monoxide to kaolin reduces

its refractoriness to Cone 30 (1670° C.), 13·73 per cent. reduces it to Cone 12 (1350° C.), and 24·15 per cent. reduces it to about Cone 1 (1100° C.). Larger percentages still further increase the fusibility of the kaolin.

Phosphorus and vanadium compounds occur in very small proportions in some clays, but these constituents are usually negligible. If in sufficient proportion to have any appreciable effect, they reduce the refractoriness of the material (see calcium phosphate (p. 367). Vanadium sometimes produces a greenish colour in burned clays (p. 123).

The effect of vanadium oxide on the refractoriness of kaolin is shown in Table CXII, due to O. Kallauner and T. Hruda.[1]

TABLE CXII.—*Effect of Vanadium on Kaolin*

Kaolin.	Vanadium Pentoxide.	Cone.	Refractoriness, ° C.
100	0	35	1770
99	1	34	1750
95	5	33	1730
90	10	32	1710
80	20	30	1670
60	40	15	1435
40	60	5*a*	1180
20	80	08*a*	940
0	100	020	675

Sulphur occurs in clays chiefly in the form of iron sulphides (pyrites), or as gypsum (calcium sulphate), though more soluble sulphates may occur to some extent either from the oxidation of sulphides or by contact with water containing sulphates in solution. When the clay is heated the sulphur compounds are usually decomposed, the sulphur being evolved as sulphur trioxide. The temperature of decomposition varies according to the nature of the compound. Thus, ferric sulphide (FeS_2) gives off half its sulphur at 400° C. and the remainder at a higher temperature ; sulphates are decomposed between 800° and 1000° C. At 700° C., in the presence of reducing gases, they are usually reduced to sulphides.

Insoluble sulphur compounds are not usually objectionable unless the material is heated until vitrification begins, when they evolve gases which may produce a spongy or " bloated " ware of greatly distorted shape. This is especially noticeable if brick clays containing iron pyrites are heated too rapidly from 500°–900° C.

Soluble sulphates are chiefly objectionable on account of the white scum they produce on the surface of the ware. This may be made less objectionable by heating the ware to such a temperature that the scum-forming compound combines with

[1] *Sprechsaal*, **45**, 333–5, 345–9 (1922).

the clay and forms a transparent colourless glaze, most of which is absorbed by the ware.

Moisture and colloidal water (p. 336) are present in natural clays in widely varying proportions. To them, the clays largely owe their plasticity and other physical properties, so that these forms of water can scarcely be regarded as impurities. A knowledge of the proportions present is very important, however, if definite quantities of different materials are to be mixed together, as in the preparation of earthenware, stoneware, or porcelain bodies and engobes, for any variation in the proportion of moisture from that which is assumed to be present will affect the amount of clay used and so may alter the properties of the materials. For this reason, a knowledge of the proportion of free water present is sometimes of great importance.

Carbonaceous matter occurs in most clays, but the proportion varies greatly, some clays containing less than 0·5 per cent., whilst others contain 5 per cent. or more. Bricks are sometimes made from " colliery refuse " containing as much as 12 per cent. of carbonaceous matter, but such materials are mixtures of clay and coal and cannot be regarded as clays. Some *indurated clays* or *shales* contain 25 per cent. of carbonaceous matter; they are chiefly used as a source of oil, which is obtained by heating them to about 500° C. and condensing the vapours evolved from them.

Carbonaceous matter in clay—(*a*) affects the colour of the raw and dry clays, but not that of the burned material unless the latter is deprived of sufficient air in the heating process; (*b*) may increase the plasticity of the clay if the carbonaceous matter is in a colloidal state, otherwise it may act as a non-plastic material and reduce the plasticity; (*c*) increases the porosity of the fired ware; (*d*) increases the permeability of the fired ware by producing relatively large pores; (*e*) may increase the amount of water absorbed by the raw clay; (*f*) may increase the shrinkage of the clay; (*g*) reduces the amount of fuel required to burn the goods; (*h*) may cause trouble in firing, as, unless special precautions are taken, black cores of charred carbonaceous matter may be left in the fired ware; these cannot be " burned out " at a temperature above 950° C., owing to the sealing of the pores at and above this temperature; (*i*) may cause the reduction of iron compounds to the ferrous state, in which case they will act as fluxes and form dark fusible silicates.

The extent of the action of carbonaceous matter depends largely on the conditions during the burning and on the texture of the clay or clay mixture. In a material which is open in texture and is heated slowly with an ample supply of air, the carbonaceous matter burns away quietly and usually does little or no harm. If the heating is effected too rapidly, so that too high a temperature is reached before all the carbonaceous matter has been burned out of the ware, the latter may be spoiled by (*a*) discoloration due to the charred carbonaceous matter which is covered by a film of fused siliceous material and so cannot be burned away, or (*b*) bloating or swelling of the ware, due to the exterior pores being sealed by fused siliceous material and so preventing the escape of the gases produced in the interior of the ware by the continued action of the heat on the carbonaceous material. The only means of preventing either of these defects consists in controlling the heating and air supply

in the kilns during the early stages of firing (*i.e.* before a temperature of 950° is reached) so as to burn off the carbonaceous matter so slowly that the temperature does not reach that at which partial fusion can occur.

Although it is usually undesirable for clays to contain more than about 5 per cent. of carbon in the form of carbonaceous matter, free carbon is sometimes added for special purposes. Thus, the presence of 15–25 per cent. of plumbago or graphite increases the resistance of firebricks or crucibles to corrosion by slags, fluxes, etc., prevents undue oxidation of the contents of crucibles, and makes such articles less sensitive to sudden changes in temperature. Coke is sometimes used instead of graphite ; though much cheaper, it is far less effective. Sawdust is sometimes added to clays to produce ware of high porosity, the pores being produced when the sawdust or other carbonaceous powder burns away. (See also Chapter X.)

The water of constitution and crystallisation of pure clay can scarcely be regarded as impurities, but when they form a part of other minerals or carbonaceous matter in a clay or clay mixture their effect may have to be taken into consideration. Water in both these forms is only evolved when the material is heated and, if the temperature rises sufficiently slowly and the kiln or furnace is well ventilated, little or no harm will be done. With too rapid heating, on the contrary, the various effects known technically as " steaming " may spoil the ware.

From the foregoing pages it will be seen that the beneficial or harmful effect of an impurity in a clay must be judged by the purpose for which the clay is to be used ; some impurities may be allowable under some conditions, but must not be present when the same clay is used for other purposes. Consequently, in selecting clays or other ceramic materials, the purposes for which they or the finished articles are to be used must always be taken into consideration.

Composition and Utility

The effect of the composition, as of the physical properties, of a clay or clay mixture on the utility of articles made from it is a matter of great technical importance. It usually determines the commercial value of the raw material as well as limiting the purposes for which it may be profitable employed. Various investigators have endeavoured to find a simple means of correlating the composition of clays with their utility, but, so far, with little success. This is only to be expected, as most natural clays are such complex mixtures of different minerals that it is unlikely that any simple ratio of two ingredients (such as silica and alumina) can accurately express their utility. All that such a ratio can indicate is the general fact that, for some articles made of mixtures of clay and silica, the proportion of each of these materials should be within certain broadly defined limits. As it is difficult to ascertain the proportion of true clay present, the assumption is usually made that the alumina is strictly proportional to the true clay and, therefore, that the ratio of silica : alumina may be taken as a rough basis of classification. When it is desired to include the other constituents (*e.g.* the bases) in such a ratio, the validity of the assumption is very questionable ; nevertheless, W. Pukall has stated that the molecular ratio

of silica : bases+alumina in ceramic bodies varies from 0·5 : 1 to 3 : 1 ; kaolins and fireclays poor in silica have ratios from 0·5 : 1 to 1 : 1, whilst many clays suitable for bricks, tiles, and terra-cotta have a ratio from 2 : 1 to 3 : 1 and the clays used for fine ceramic wares generally have a ratio between 1 : 1 and 2 : 1.

China clay and **kaolins,** when pure, contain about 46 per cent. of silica, 40 per cent. of alumina, and 14 per cent. of water. The best commercial samples contain about 45 per cent. of silica, 39 per cent. of alumina, 13 per cent. of water, and 3 per cent. of other oxides, notably lime, magnesia, soda, potash, iron, and titanium oxides. It must be remembered, however, that 3 per cent. of impurities in the form of fluxing oxides may be equivalent to 10 per cent. of the total impurity in the material, the other 7 per cent. being included in the figures for silica and alumina, because many impurities do not occur as simple oxides, but as silicates and alumino-silicates, such as felspar, mica, etc. Kaolins containing more than 4 per cent. of alkalies are termed alkaline kaolins. The greater part of the alkali-bearing minerals may, in some cases, be removed by careful preparation and washing. Ferruginous kaolins contain a large proportion of iron oxide and, consequently, are not so white when burned as are pure varieties.

For pottery manufacture, china-clay should not usually contain more than 0·5 per cent. of lime, though some foreign kaolins contain up to 3 per cent. ; for paper-making, the composition is of minor importance if the clay is sufficiently white and plastic. Magnesia may occur in proportions from 0–3 per cent., but in the best qualities not more than 0·2 per cent. should be present. Free silica should not be present in the best china clay or kaolin to a greater extent than 10 per cent., though some commercial samples and some siliceous kaolins contain as much as 25 per cent. of fine grains of silica.[1]

Ball clays and **pottery clays** are similar in chemical composition to china clays, but contain more alkalies and iron oxide. The following composition is typical of high-class ball clays :—

Silica	40–48 per cent.
Alumina	32–36 per cent.
Iron oxide	Less than 2 per cent.
Lime, Magnesia	Less than 1 per cent.
Potash, Soda	Less than 3 per cent.

Pottery clays usually contain 45–86 per cent. of silica, the average being about 48 per cent. ; 7 per cent. of alkalies is sometimes present, but the proportion is not generally more than about 2 per cent. Not more than 2 per cent. of lime and about 1 per cent. of magnesia should be present, less than these amounts being usually desirable. The iron oxide should be as low as possible so as to prevent the discoloration of the burned clay.[1]

[1] Further analyses of china clays and ball clays will be found in the author's *Refractory Materials : Their Manufacture and Uses* (Griffin).

Fireclays vary greatly in composition, and may contain 34–98 [1] per cent. of silica, the average being about 54 per cent., but the best qualities are those in which the percentage of silica is not much greater than that of the alumina, as these contain the largest proportion of true clay. The Institution of Gas Engineers has specified that fireclays should not usually contain more than 75 per cent. of silica, though in some cases 80 per cent. may be present, provided the material fulfils all the other requirements of the Institution's specification.

The American Gas Institute has specified 75 per cent. of silica as the maximum amount allowable in articles to be sold as "fireclay bricks"; those containing a larger percentage of silica are termed "siliceous bricks."

Fireclays should not usually contain more than about 2 per cent. of potash and soda, though in some cases 5 per cent. may be present without having any serious effect on the quality. Bleininger and Brown [2] have suggested that for each one molecule of alumina the proportion of fluxes should not exceed 0·225 molecular equivalents in a refractory clay.

Fireclays should not contain a large proportion of lime, as this is a very powerful flux. Some contain as much as 10 per cent., but this is much too high for a refractory clay, the average being about less than 2 per cent.

The proportion of magnesia seldom exceeds 6 per cent., equivalent to about 12 per cent. of magnesite, and averages about 0·5 per cent. Several good fireclays in this country contain 3 per cent. of magnesium carbonate.

The proportion of iron compounds in the best fireclays should not exceed 2 per cent., expressed as ferric oxide: some of the less pure ones contain 5 per cent. In America, some fireclays are used containing as much as 7 per cent. of iron oxide. The so-called Windsor firebricks, which are made from a soft red sandstone, contain about 4·5 per cent. of iron oxide, but are sufficiently refractory for gas-retort settings, etc., provided they are used in an oxidising atmosphere, so that the iron remains in the ferric state. When heated under reducing conditions the iron combines with the silica and forms a fusible slag.

The Ewell bricks—made at Ewell, in Surrey—and similar bricks made at Chalfont St Peter, are used for the same purposes as bricks made of Windsor loam; they consist of—

Silica . . .	84·65 per cent.
Alumina . . .	8·85 ,,
Lime . . .	1·90 ,,
Magnesia . .	0·35 ,,
Iron oxide . .	4·25 ,,

Riley [3] appears to have been one of the first chemists to find titanium oxide in English fireclays and in many more recent analyses this constituent is not mentioned, being included in the figures for silica and alumina. The proportion of titanium

[1] The application of the term "fireclay" to a material containing 90 per cent. or more of silica is a misnomer.

[2] *Loc. cit.*, p. 149.

[3] *Quart. J. Chem. Soc.*, **15**, 311 (1862).

oxide in English fireclays is generally less than 2½ per cent., whilst some American clays contain nearly 5 per cent., though these are abnormal, the usual proportion being less than 2 per cent. A few clays have been found with 10 per cent. of titanium oxide. Further analyses of various fireclays will be found in the author's *Refractory Materials: Their Manufacture and Uses* (Griffin).

Brick clays depend for their value on their physical properties rather than on their chemical composition and, consequently, the permissible range of composition of brick clays is very wide. The clays used for building bricks may have from 35–90 per cent. of silica, the average being between 60 and 70 per cent. of silica. If the true clay present is sufficiently plastic, good bricks can usually be made from a material consisting essentially of about 50 per cent. of such true clay and 50 per cent. of silica; this would correspond to about 73 per cent. of silica in the mixture. So small a proportion of clay can only be satisfactory when the true clay is exceptionally plastic; otherwise, the bricks would be too weak to be satisfactory.

Brick clays (with the exception of those used for firebricks) may usually contain a comparatively large proportion of metallic oxides (fluxes), as they are not heated to a sufficiently high temperature to cause distortion due to excessive fusion. In the absence of a moderate proportion of these oxides, the brick will be deficient in vitrifiable bonding material, and so will be relatively weak. With a suitable proportion of fluxes bricks of enormous strength can be produced, each particle of unfused material being held in place by the crude glass formed when the fluxes combine with the silica in the clay. Clays suitable for building bricks may contain up to 15 per cent. of alkalies (the average being about 3 per cent.), up to 15 per cent. of calcium compounds expressed as lime (the average being below 2 per cent.), and up to 7 per cent. of magnesia (the average being about 1 per cent.). Iron compounds (expressed as ferric oxide) occur in proportions up to 32 per cent., the average being 3–8 per cent.; the red colour of many bricks is due to the fully-oxidised iron compounds present and the colour of "blue" bricks to the reduced iron compounds present. Further analyses of brick clays will be found in the author's *Modern Brickmaking* (Scott, Greenwood & Son).

Some clays which shrink excessively, and others which have a poor colour when burned, are improved by the addition of sand, especially if this contains a considerable proportion of iron compounds other than pyrites.

The metallic compounds most likely to cause trouble in the manufacture of building bricks are (*a*) lime compounds and (*b*) "soluble salts." The lime compounds produce lime which slakes and may crack the bricks containing it. This may be largely avoided by grinding the limestones to a fine powder, as particles of limestone less than 0·04 inch in diameter seldom crack bricks containing them. In some works, washed chalk (calcium carbonate) is purposely added to bricks to reduce the shrinkage of the clay and to act as a binding agent.

Soluble salts are chiefly objectionable because they form a white efflorescence or "scum"; consequently, brick clays containing an appreciable proportion of soluble salts can only be used where the appearance of the fired bricks is of no importance.

Fine earthenware necessarily requires clays which are sufficiently white when

burned, though by using a sufficient proportion of flint or other suitable non-plastic material it is often possible to make good use of a clay which is not sufficiently white when used alone. Various blue colours may also be used to destroy the yellow colour of some burned clays. In England, the clays used for fine earthenware are chiefly ball clay and china clay, but in some Continental works red-burning clays mixed with chalk or finely-ground limestone are used. The product is white, as calcium carbonate has a powerful bleaching action on red-burning clays.

Earthenware—whether fine or coarse—is porous except for the glaze and it is, in this way, distinguished from porcelain and other dense ware.

Coarse earthenware may be made of almost any clay which can be made into articles of the desired shape. The colour of the burned clay may be disguised, if required, by covering the ware with a suitable engobe or an opaque glaze.

China ware and **porcelain** are made of mixtures of various white-burning clays and fluxes of such a nature and in such proportions as will produce a dense, vitreous, and translucent body. China ware is made of china clay, ball clay, flint, bone ash, and Cornish stone; it owes its translucency largely to the formation of a glassy binding material formed by the combination of bone ash and silica. Such ware usually varies in composition between the following limits :—

$$1{\cdot}15\text{–}8{\cdot}33RO\ Al_2O_3\ 1{\cdot}97\text{–}9{\cdot}08SiO_2\ 0{\cdot}35\text{–}2{\cdot}67P_2O_5.$$

Ideal porcelain should consist of a mixture corresponding to the formula $Al_2O_3SiO_2$ (sillimanite) and a fusible glass which binds the other particles firmly together. When materials capable of producing such a mixture are heated to a sufficiently high temperature they will form a felted mass of sillimanite needles bonded with a glassy cement. A perfect porcelain is seldom obtained, though Marquardt's porcelain approaches very closely to it.

There are at least five distinct types of porcelain and the clays used for one type are not necessarily suitable for another.

1. *Sèvres porcelain* is made essentially of a mixture of clays and fluxes which are intended to form a special kind of glass, the chief materials being white-burning kaolin, felspar, and quartz. Sèvres porcelain corresponds approximately to the formula, $0{\cdot}30\text{–}0{\cdot}35RO\ R_2O_3\ 2{\cdot}8\text{–}3{\cdot}5SiO_2$. The Meissen and Viennese porcelains are similar in composition to that of Sèvres.

2. *Hard-paste porcelain*, including *porcelaine dure*, *Halle porcelain*, and *Berlin porcelain*, corresponding approximately to the formula, $0{\cdot}2\text{–}0{\cdot}3RO\ R_2O_3\ 4{\cdot}2\text{–}4{\cdot}8SiO_2$. The varieties of hard-paste porcelain consist essentially of a " skeleton " of unfused material saturated with glassy matter, some of the latter forming a felted mass of crystals of sillimanite on cooling. Such porcelains are peculiarly resistant to sudden changes in temperature and in this way are quite distinct from others.

3. *Soft porcelain* or *porcelaine tendre*, corresponding to the formula, $0{\cdot}4\text{–}0{\cdot}45RO\ R_2O_3\ 4{\cdot}8\text{–}5{\cdot}3SiO_2$. This is really a complex glass and the chief difficulty attending its manufacture lies in the facility with which it loses shape in the kiln owing to a deficiency of sillimanite, or of the materials from which this substance can be formed, during the conditions of manufacture.

4. *Chinese and Japanese porcelains* vary so greatly in composition and are so complex in character owing to the very impure materials used, that they can scarcely be said to correspond to any formula, though they are chiefly within the following limits :—

Japanese	$0{\cdot}3$–$0{\cdot}4RO\ Al_2O_3\ 6{\cdot}2$–$7{\cdot}4SiO_2$.
Chinese	$0{\cdot}4$–$0{\cdot}45RO\ Al_2O_3\ 5{\cdot}5$–$6SiO_2$.
Sèvres imitation of Oriental porcelain .	$0{\cdot}37RO\ Al_2O_3\ 5{\cdot}15SiO_2$.
Seger's ,, ,, ,, .	$0{\cdot}36RO\ Al_2O_3\ 8{\cdot}55SiO_2$.

5. *Dental porcelains* vary greatly in composition, some being highly refractory and others very fusible. The following typical formulæ are due to A. S. Watts [1] :—

$$(a)\quad \left\{\begin{matrix}0{\cdot}74K_2O\\0{\cdot}26Na_2O\end{matrix}\right\}1{\cdot}14Al_2O_3\ \left\{\begin{matrix}7{\cdot}830SiO_2\\0{\cdot}002TiO_2.\end{matrix}\right.$$

$$(b)\quad \left\{\begin{matrix}0{\cdot}638R_2O\\0{\cdot}141Na_2O\\0{\cdot}221CaO\end{matrix}\right\}\begin{matrix}0{\cdot}565Al_2O_3\\\\0{\cdot}090Fe_2O_3\end{matrix}\ \left\{\begin{matrix}5{\cdot}90SiO_2\\0{\cdot}023B_2O_3\\0{\cdot}011TiO_2.\end{matrix}\right.$$

$$(c)\quad \left\{\begin{matrix}0{\cdot}295K_2O\\0{\cdot}650Na_2O\\0{\cdot}055CaO\end{matrix}\right\}0{\cdot}086Al_2O_3\ \left\{\begin{matrix}4{\cdot}544SiO_2\\0{\cdot}706B_2O_3.\end{matrix}\right.$$

Many attempts have been made to produce hard-paste porcelain at lower temperatures than that required for the best qualities of this material. Thus, Pukall gives the following typical composition for porcelains maturing at Cone 7 (1230° C.) :—

$$\left\{\begin{matrix}0{\cdot}5K_2O\\0{\cdot}5CaO\end{matrix}\right\}Al_2O_3\ 5SiO_2.$$

Dorfner prefers a material containing more alumina and silica and corresponding to

$$\left\{\begin{matrix}0{\cdot}65K_2O\\0{\cdot}35CaO\end{matrix}\right\}1{\cdot}97Al_2O_3\ 11{\cdot}68SiO_2$$

and Hertwig-Möhrenbach [2] has suggested the following limits of composition for porcelains maturing at Cone 9 :—

$$RO\ 3Al_2O_3\ 14{\cdot}45SiO_2 \text{ to } RO\ 4{\cdot}8Al_2O_3\ 27SiO_2.$$

The ware corresponding to the lower limit is not very translucent, as most of the vitrified material is only formed at a much higher temperature, but that corresponding to the upper limit is highly translucent. The former, if fired at Cone 14, produces translucent ware.

The materials used for the production of all these porcelains are china clay or kaolin, felspar (or some equivalent mineral such as china stone or pegmatite), and free silica in the form of crushing quartz or calcined flint. These materials must be

[1] *Trans. Amer. Cer. Soc.*, **17** (1915).
[2] *Sprechsaal*, **53**, 363–5 (1920).

very finely divided and extremely well mixed so as to ensure the steady and regular progress of the chemical reactions between the constituents and the uniform progress of the physical changes which take place when they are heated. Otherwise, distortion of the ware will occur. The materials must be sufficiently uniform in composition to enable successive batches to produce ware having the same characteristics, though some adjustment is possible by varying the proportions of each material in the mixture. The materials must be sufficiently free from iron and other discolouring impurities to enable white ware to be produced. Slight differences in the materials from various sources, as well as slight variations in the proportions in which they are used, largely account for the differences between specimens of porcelain and china ware from different factories.

One of the remarkable features of the older Chinese porcelains is the manner in which very crude and impure materials have been used to produce a ware of extraordinary technical and artistic quality. The very serious complexities thus introduced add greatly to the æsthetic value of such ware.

The chief purpose of the clay and some of the free silica in all porcelain is to produce the felted mass of sillimanite crystals which form the " skeleton " of the finished ware and to provide a " reinforcement " which will prevent undue distortion of the ware. The other ingredients have two purposes : (*a*) part of them commence to fuse at a comparatively early stage in the firing and so produce a solvent for the remainder, and (*b*) these ingredients, together with the clay and free silica, combine to form a glassy fluid—which must be produced slowly and progressively to avoid loss of shape in the ware—from which the sillimanite may crystallise, the remaining material forming the vitrified magna to which—with the sillimanite—porcelain owes its peculiar characteristics.

The nature of the fluxes in porcelains, etc., is very important, as upon them the nature of the finished products largely depends. H. Hope [1] has given the following summary of the effect of various fluxes upon white porcelain mixtures :—

Lime, or its equivalent, gives a strong porcelain with moderate shrinkage and only a slight tendency to blister, but the colour of the ware is rather poor.

Magnesia tends to cause blisters, but if less than 0·1 equivalents are present, this is not serious ; the colour of the ware is usually very good.

Strontia has the least tendency to blister and gives a strong ware with high porosity and low shrinkage ; the colour of the ware is fairly good.

Barium oxide gives a weak body, with excessive shrinkage and blistering. The translucency of the ware is better than other fluxes, but the colour is poor.

Zinc oxide produces ware of a very good colour, even in small quantities, but with more than 0·05 equivalents there is sometimes a bluish or greenish tinge. With 20 per cent. of felspar, zinc oxide gives a good strong body, but with more than 0·02–0·03 equivalents of zinc oxide the ware tends to opacity and there is a tendency to " shivering."

Soda and potash—preferably in the form of felspar—are the best fluxes for porcelain.

[1] *Trans. Amer. Cer. Soc.*, **11**, 494 (1909).

Table CXIII shows the chemical composition, and Table CXIV the mixtures used for various porcelains.

TABLE CXIII.—*Chemical Composition of Porcelains*

Porcelain.	Silica.	Alumina.	Ferric Oxide.	Potash.	Soda.	Lime.	Magnesia.	Titanium Oxide.	Borax.	Loss.
Sèvres (1848)	59·2	35·2	..	3·2	..	3·4	..	..	..	..
Dental [1] A.	68·2	16·7	trace	10·1	2·3	..	..	0·23	..	2·5
,, B.	68·1	2·2	..	6·9	10·1	0·8	..	trace	10·6	1·2
,, C.	69·6	11·3	0·3	11·8	1·7	2·4	..	0·2	0·3	..
Meissen .	58·5	35·1	0·8	5·0	..	0·3	0·6	..	..	..
Vienna .	59·6	34·2	0·8	2·0	..	1·7	1·4	..	..	..
Berlin .	64·3	29·0	0·6	3·6	2·7	0·3	0·5	..	..	..
China .	70·0	22·2	1·3	3·6	2·7	0·8	..	..	..	..
Refractory	61·6	30·0	1·56	3·26	..	3·56	..	..	..	..

TABLE CXIV.—*Mixtures Used for Various Porcelains*

Porcelain.	Sèvres.	Berlin.	Chinese.	Seger.	Bone China.			Dental.[1]			Chemical.	Parian Ware.		
					A.	B.	C.	A.	B.	C.		A.	B.	C.
Kaolin . .	38	77	47	13·0	33–35	26	30	4	..	..	} 80	1	1	40
Ball clay . .	..	..	..	15·5	..	..	..	..	..	..				
Felspar . .	38	23	15	30·0	15–19	..	..	81	61	12	10	2	2	58
Cornish stone .	..	..	..	..	..	30	35	..	..	..	..	..	..	..
Flint . . .	..	..	..	..	10–14	..	..	15	29	60	..	..	..	..
Quartz . . .	24	..	38	41·5	..	..	..	..	..	..	10	..	3	..
Bone ash . .	..	..	..	..	32–42	44	35	..	..	..	..	..	..	..
Sodium carbonate .	..	..	..	..	..	..	..	..	2	8	..	..	..	..
Borax . . .	..	..	..	..	..	..	..	..	1	11	..	..	..	..
Calcium carbonate .	..	..	..	..	..	..	..	..	5	1	..	..	..	..
Potassium ,, .	..	..	..	..	..	..	..	..	2	8	..	..	..	..

Magnesic porcelains usually consist of magnesia, alumina, and some silica. The two latter being in the form of clay, though Heinecke's magnesic porcelain consists of powdered alumina and magnesia bonded with dextrin, no silica or clay being used.

Steatite porcelain consists of a mixture of natural magnesium silicate (steatite),

[1] Formulæ on p. 376.

together with clay, felspar, and flint, though in some cases steatite is used alone in the form of a fine dust, which is moulded under great pressure. Fused steatite has also been used by the British Thompson-Houston Company.

Seger cones are made of artificial mixtures similar to porcelains. Table CXV shows their chemical composition as originally proposed by Seger, but the estimated temperature which they indicate is derived from later determinations in 1908 by Simonis.

TABLE CXV.—*Composition of Seger Cones*

Potash.	Soda.	Lime.	Lead Oxide.	Alumina.	Iron Oxide.	Silica.	Boric Oxide.	Cone No.	Estimated Temperature, ° C.
..	0·5	..	0·5	..	..	2	1	022	600
..	0·5	..	0·5	0·1	..	2·2	1	021	650
..	0·5	..	0·5	0·2	..	2·4	1	020	670
..	0·5	..	0·5	0·3	..	2·6	1	019	690
..	0·5	..	0·5	0·4	..	2·8	1	018	710
..	0·5	..	0·5	0·5	..	3	1	017	730
..	0·5	..	0·5	0·55	..	3	1	016	750
..	0·5	..	0·5	0·6	..	3·2	1	015	790
..	0·5	..	0·5	0·65	..	3·3	1	014	815
..	0·5	..	0·5	0·7	..	3·4	1	013	835
..	0·5	..	0·5	0·75	..	3·5	1	012	855
..	0·5	..	0·5	0·8	..	3·6	1	011	880
0·3	..	0·7	..	0·3	0·2	3·50	0·45	010	900
0·3	..	0·7	..	0·3	0·2	3·55	0·50	09	920
0·3	..	0·7	..	0·3	0·2	3·60	0·40	08	940
0·3	..	0·7	..	0·3	0·2	3·65	0·35	07	960
0·3	..	0·7	..	0·3	0·2	3·70	0·30	06	980
0·3	..	0·7	..	0·3	0·2	3·75	0·25	05	1000
0·3	..	0·7	..	0·3	0·2	3·80	0·20	04	1020
0·3	..	0·7	..	0·3	0·2	3·85	0·15	03	1040
0·3	..	0·7	..	0·3	0·2	3·90	0·10	02	1060
0·3	..	0·7	..	0·3	0·2	3·95	0·05	01	1080
0·3	..	0·7	..	0·3	0·2	4	..	1	1100
0·3	..	0·7	..	0·4	0·1	4	..	2	1120
0·3	..	0·7	..	0·45	0·05	4	..	3	1140
0·3	..	0·7	..	0·5	..	4	..	4	1160
0·3	..	0·7	..	0·5	..	5	..	5	1180
0·3	..	0·7	..	0·6	..	6	..	6	1200
0·3	..	0·7	..	0·7	..	7	..	7	1230

TABLE CXV.—*Composition of Seger Cones (continued)*

Potash.	Soda.	Lime.	Lead Oxide.	Alumina.	Iron Oxide.	Silica.	Boric Oxide.	Cone No.	Estimated, Temperature C.°
0·3	..	0·7	..	0·8	..	8	..	8	1250
0·3	..	0·7	..	0·9	..	9	..	9	1280
0·3	..	0·7	..	1·0	..	10	..	10	1300
0·3	..	0·7	..	1·2	..	12	..	11	1320
0·3	..	0·7	..	1·4	..	14	..	12	1350
0·3	..	0·7	..	1·6	..	16	..	13	1380
0·3	..	0·7	..	1·8	..	18	..	14	1410
0·3	..	0·7	..	2·1	..	21	..	15	1435
0·3	..	0·7	..	2·4	..	24	..	16	1460
0·3	..	0·7	..	2·7	..	27	..	17	1480
0·3	..	0·7	..	3·1	..	31	..	18	1500
0·3	..	0·7	..	3·5	..	35	..	19	1520
0·3	..	0·7	..	3·9	..	39	..	20	1530
0·3	..	0·7	..	4·4	..	44	..	21	
0·3	..	0·7	..	4·9	..	49	..	22	Not manufactured.
0·3	..	0·7	..	5·4	..	54	..	23	
0·3	..	0·7	..	6·0	..	60	..	24	
0·3	..	0·7	..	6·6	..	66	..	25	
0·3	..	0·7	..	7·2	..	72	..	26	1580
0·3	..	0·7	..	20·0	..	200	..	27	1610
..	..	..	..	1	..	10	..	28	1630
..	..	..	..	1	..	8	..	29	1650
..	..	..	..	1	..	6	..	30	1670
..	..	..	..	1	..	5	..	31	1690
..	..	..	..	1	..	4	..	32	1710
..	..	..	..	1	..	3	..	33	1730
..	..	..	..	1	..	2·5	..	34	1750
..	..	..	..	1	..	2	..	35 [1]	1770
..	..	..	..	1	..	2	..	36 [2]	1790
..	..	..	..	1	..	1·66	..	37	1825
..	..	..	..	1	..	1·33	..	38	1850
..	..	..	..	1	..	1	..	39	1880
..	..	..	..	1	..	0·66	..	40	1920
..	..	..	..	1	..	0·33	..	41	1960
..	..	..	..	1	..	..	..	42	2000

[1] Kaolin.

[2] Clay schist.

Chemical Composition and Refractoriness.—Many attempts have been made to find a definite relation between the composition of clays and their refractoriness. So far it has been found impossible to find any definite rule which can be applied to all clays, but with the purer clays, such as the fireclays and kaolins, where there are fewer factors to be considered, a definite relation has been found to exist.

Simonis attempted to establish a relation between the refractoriness of mixtures of kaolins, quartz, and felspar, and taking R as the proportion of kaolin, S the percentage of silica, and f the percentage of felspar, he deduced two "refractory indices," viz. $R = \frac{S}{3} - f + 60$ (where $k > \frac{S}{3}$), and $R = \frac{2S}{3} - k + 60$ (where $\frac{S}{3} > k$). The refractory index expressed in terms of Seger cones is shown in Table CXVI.

TABLE CXVI.—*Refractory Indices and Seger Cones*

Cone.	Refractory Index.	Cone.	Refractory Index.
14	17·5	27	65
15	22·6	28	72
16	28·0	29	80
17	33·7	30	89
18	39·2	31	102
19	44·6	32	114
20	50·0	33	127
26	57·6	34	141

Bischof's "refractory coefficient" is found by dividing the alumina : silica ratio by the fluxes : alumina ratio, *i.e.* where a is the amount of oxygen in the alumina, b the amount of oxygen in the silica, and c that in the fluxes $\times 3$.

$$\text{Refractory coefficient} = \frac{a}{b} \div \frac{c}{a} \text{ or } \frac{a^2}{bc}.$$

This coefficient does not take into account various physical factors which are of great importance in deciding the refractoriness and so is seldom correct, except when limited to highly refractory clays ; it is not applicable to second-grade fireclays and clays used for building purposes.

Seger has suggested a modification of Bischof's formula, viz. :

$$Q = (a + b)\frac{a}{b},$$

where Q is the "refractory coefficient," and a and b bear the same significance as in

Bischof's formula. The fluxes *c* are not considered, as the formula applies only to very pure clays.

The formulæ suggested by Bischof and Seger are not satisfactory as they can only be employed within very small ranges of composition ; the chart prepared by Ludwig (fig. 21) is surprisingly accurate within much wider limits. Ludwig based his chart on the assumption that clays are solid solutions of the minerals constituting the " impurities " in the clay and that they must, therefore, reduce the melting-point of the clay in proportion to their molecular concentration. He determined the refractoriness of many clays of different composition and then calculated their formula, assuming the alumina to be unity, *i.e.* $x\mathrm{ROAl_2O_3}y\mathrm{SiO_2}$. He then marked off the

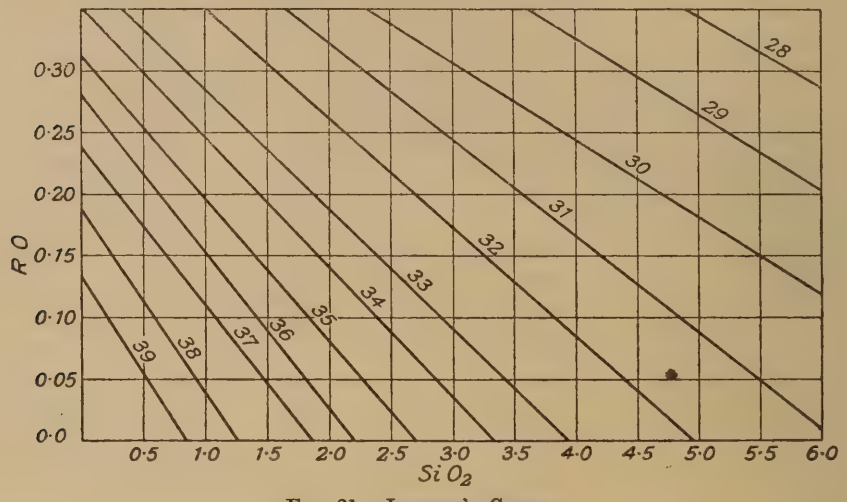


Fig. 21.—Ludwig's Chart.

refractoriness of the clays on a graph having the molecular ratios of RO as ordinates and those of SiO_2 as abscissæ. When the iso-refractory lines corresponding to the various Seger cones are plotted on the graph, they enable the refractoriness of any material of a composition lying on or between any of these lines to be ascertained with a fair degree of accuracy. This chart is very useful for clays containing up to 6 per cent. of RO bases, but for less pure clays it is useless, on account of the heterogeneous nature of the materials.

THE CHEMICAL COMPOSITION OF ENGOBES AND GLAZES

The subject of engobes and glazes cannot be fully dealt with in this volume, as it would require a volume to itself, so diverse are the manifold possible compositions. It is only possible, therefore, in the following pages to give a general idea of their chemical composition, their adaptation for special purposes, and some of the methods of avoiding defects.

Engobes or **bodies** are of extremely variable composition and it is impossible

to give figures of general application, as each engobe must be modified so as to adhere well to the body upon which it is to be placed. Engobes usually consist of a mixture of white-burning clay and flint, together with at least two fluxes, the proportions of these ingredients being modified so as to secure a covering which has a contraction identical with that of the ware to which it is applied. In some cases, lime is used as the only flux, but two fluxes are generally desirable, as they produce a more stable "glass" which binds the particles of clay more firmly together than when only one flux is present. Hence, many engobes contain a considerable proportion of felspar or Cornish stone, which incidentally provides potash—an excellent flux. Two typical engobes with one flux correspond to the formulæ :

(i) $CaO\ 0{\cdot}5Al_2O_3\ 4SiO_2$;
(ii) $0{\cdot}15K_2O\ Al_2O_3\ 5SiO_2$.

A widely used engobe, with two fluxes maturing at Cone 4, corresponds to the formula :

$$\left.\begin{matrix}0{\cdot}7CaO\\0{\cdot}3K_2O\end{matrix}\right\}0{\cdot}5Al_2O_3\ 4SiO_2.$$

The chemical composition of engobes is of minor importance compared with that of glazes, as the former are essentially mixtures of clay and vitrifiable matter, and their most important characteristics are physical, viz. (i) a suitable appearance (usually a perfect white) when fired, and (ii) complete adhesion to the ware to which they are attached.

Glazes may be divided—so far as their chemical composition is concerned —into

(*a*) *Alkaline glazes*, consisting chiefly of silicates of potash and soda ; the most important of these are *salt glaze* and some of the unstable glazes occasionally used for ornamental ware and enamels.

(*b*) *Felspathic glazes*, consisting of silica and alumina, with alkaline or alkali-earthy bases.

(*c*) *Lead glazes*, which may consist of (i) a simple lead silicate, or (ii) a glaze similar to felspathic glazes, but having their melting-point reduced by the addition of lead compounds.

(*d*) *Enamels*, which are ordinary lead or felspathic glazes rendered opaque by the addition of tin oxide or other opacifying agent. (Unfortunately, the term enamel is also used for transparent glazes applied to metals, but in the pottery industry its use is largely confined to opaque glazes.)

In order that it may be satisfactory, a glaze must possess three characteristics : (*a*) it must be of the right character as regards transparency or opacity and colour ; (*b*) it must be perfectly adapted to the body or ware to which it is applied so as to avoid crazing or peeling ; (*c*) it must possess a suitable fusibility in order that it may mature at a convenient temperature and one suitable to the ware to which the glaze is applied.

These characteristics are secured by suitably modifying the chemical composition

of the glaze-mixture. All these characteristics are equally important and yet, in some cases, they are incompatible, so that various compromises must be effected.

An increase in transparency is usually obtained by making the glaze more fusible or by reducing the proportion of non-fusible matter in it. The adhesion of a glaze to the ware may sometimes be increased by adding clay (though this may make it less transparent), by making it more fusible (though this may cause " crazing "), or by varying the proportions of the various minerals in such ways as previous experience may suggest.

The effect of composition upon the fusing-point of glazes is a subject of very great complexity and whilst an increase in the proportion of bases will usually make a glaze more fusible, and an increase in the proportion of flint or clay will usually make the glaze less fusible, no general rule is equally accurate in all cases, as so much depends on the mutual reactions of the different materials. Thus, if a glaze is of such a composition that all the bases are suitably combined with silica and alumina, the addition of an acid material, such as flint, would make the glaze less fusible, roughly, in proportion to the amount added. If, however, the glaze contained some uncombined base, such as whiting, on account of the lack of acidic matter to combine with it, the addition of such a material as flint would enable further combination to occur and the glaze would be made more fusible, thereby appearing to contradict the general rule that the addition of a base increases the fusibility of a glaze.

There can be no definite relationship between the fusibility and composition of a glaze, because the fusing-point of a glaze depends upon—

(*a*) The molecular ratio of fluxing bases (RO) to silica.

(*b*) The nature of the fluxes.

(*c*) The molecular ratio of the alumina to the fluxes and to the silica.

(*d*) The ratio of the silica to boric oxide if present.

The only certain method is first to study the molecular proportions of the various RO bases and silica in a glaze (the Al_2O_3 being taken as unity) and then, having obtained a good general idea by this means, to carry out a series of experiments. It frequently happens that unexpected eutectic compounds are produced and these upset any predictions from the chemical formulæ.

Various investigators have suggested that the behaviour of glazes is dependent to a large extent on the ratio between the oxygen in the bases and that in the acid (chiefly silica) portions of the glazes. Thus, Seger pointed out that crazing may sometimes be prevented by increasing the value of the ratio $\frac{\text{oxygen in silica}}{\text{oxygen in bases}}$, but this does not adequately allow for the effect of alumina.

Hopkins [1] has pointed out the importance of considering the atomic volumes of the bases present in glazes and suggests that crazing is most likely to occur when the ratio

$$\frac{\text{atomic volume of oxygen in the basic oxide}}{\text{atomic volume of basic element in the oxide}}$$

[1] *Trans. Eng. Cer. Soc.*, **9**, 120 (1909–10).

is low. This figure he terms the oxygen strain. The atomic volumes of the principal elements considered by Hopkins are as follows :—

Zn	. .	atomic volume,	9·2	Ba	. .	atomic volume,	36·7
Na	. .	,, ,,	23·7	K	. .	,, ,,	47·0
Ca	. .	,, ,,	28·3	O	. .	,, ,,	14·3

J. W. Mellor has pointed out that Hopkin's theory does not apply to glazes containing copper, which has an atomic volume of 7·1, but is not superior to zinc as an anti-craze. This theory also does not agree with the work of Damour and Hovestadt, who give, respectively, the following orders :—

$ZnO, PbO, CaO, CuO, BaO, Na_2O$
$ZnO, PbO, BaO, CaO, K_2O, Na_2O$

for the influence of bases on the coefficient of expansion of glass.

Influence of Constituents on Engobes and Glazes

The following information on the influence of various constituents of engobes and glazes is sometimes useful in determining the probable effect of altering the composition of a given engobe or glaze.

Silica is used in glazes to supply the chief acid radicle and also to regulate the temperature at which a glaze will mature. An excess of silica, which remains unaltered in the glaze, decreases its transparency and prevents complete fusion except at a higher temperature. On the other hand, a deficiency of silica reduces the ductility of a glaze and imparts a tendency for it to boil and blister.

Purdy [1] has found that a high proportion of flint causes "shivering," the effect being greatest as the temperature rises from Cones 5–11. Ware containing 30–50 per cent. of flint, when fired at a temperature above Cone 5, will not shiver or craze from this cause. A low proportion of flint and a high proportion of clay will cause crazing irrespective of the proportion of felspar present.

Alumina often acts as a base in glazes, but it does not influence the fusing-point to any great extent. Its chief value is to permit considerable variations in the composition and firing of the glaze without greatly altering its physical properties ; it is particularly useful in preventing crystallisation. It also acts as a clarifier and is especially necessary in lime glazes, where it is required in considerable proportion to prevent turbidity. In lead glazes, it has the opposite effect and causes turbidity, so that the minimum amount possible should then be allowed.

Alumina tends to reduce crazing in fritted glazes and acts similarly to silica and boric acid together, though more powerful than either of these two when used alone. Alumina cannot, according to Purdy and Fox,[2] wholly prevent crazing, unless the ratio of bases to acid is at least 1 : 2·5 and, according to these observers, when less than 0·25 equivalents of alumina are present, crazing occurs quite apart from the oxygen ratio.

W. Scheffler has stated that more than 0·4 equivalents of alumina are undesirable

[1] *Trans. Amer. Cer. Soc.*, **13**, 157 (1911). [2] *Ibid.*, **9**, 95 (1907).

in ordinary glazes and that an excess tends to increase the viscosity of the glaze and prevents the elimination of air bubbles. According to Purdy and Fox, alumina stiffens fritted glazes and raises the fusing temperature when 0·25–0·3 equivalents of alumina are present. With a smaller proportion, the opposite effect is noticed.

Keeler [1] has observed the following effects of varying the ratio of alumina : silica in terra-cotta glazes :—

Alumina : Silica Ratio.	Product.
High alumina, low silica	Immature glazes in most cases. If they do fuse, they tend to flaw and craze.
Low alumina, low silica	Crazing, pinholes, immaturity.
High alumina, high silica	Beading, immaturity, waviness, but no crazing.
Low alumina, high silica	Fair bright glazes, with tendency to waviness.

Clay is used in glazes to supply alumina and to give the requisite adhesion to the ware. On account of its alumina content it is often effective in preventing crazing. Its chief value is that, being composed of very small particles, it combines more rapidly with some of the bases. An excess must be avoided, as it makes glazes opaque.

Fluxes are employed in glazes to produce a material having the required fusing-point and transparency. The choice of the fluxes is very important ; two or more being preferable to one flux, as explained on p. 383.

In most leadless glazes, the fluxes are soda and potash, with the addition, in some cases, of magnesia, baryta, or zinc oxide.

Seger gives the following as the order of strength of various fluxes in glazes :—

TABLE CXVII.—*Fluxing Power of Glaze Fluxes*

Fluxes in Glazes (Order of Activity).	Fluxing Power of Colouring Oxides (Order of Activity).	Fluxes in Glazes (Order of Activity).	Fluxing Power of Colouring Oxides (Order of Activity).
Lead.	Manganese oxide.	Zinc.	Chromium oxide.
Baryta.	Cobalt oxide.	Lime.	Nickel oxide.
Soda.	Iron oxide.	Magnesia.	
Potash.	Uranium oxide.	Alumina.	

It is desirable to have at least two bases in a glaze, and preferably three. Lead glazes are the only exceptions to this rule, for, owing to the peculiar behaviour of lead compounds with silica one flux is sufficient, as it is easily possible to make glazes

[1] *Trans. Amer. Cer. Soc.*, **18**, 282 (1916).

of a mixture of lead oxide and silica without any other additions. Yet even in lead glazes it is often convenient to use a second base or flux. The fact that several fluxes produce a more fusible mixture than an equivalent proportion of one flux is due to the well-known law that one gram-molecule of a substance dissolved in any solvent causes a constant depression of the fusion-point, so that if several bases are present, each acts independently and the fusion-point is depressed to a correspondingly greater extent than that caused by an equivalent proportion of only one flux.

Soluble bases should, as far as possible, be avoided, as they necessitate the fusion of the base with silica, known as "fritting," which is both troublesome and costly, in order to produce an insoluble material. Soluble salts do not remain distributed uniformly through a glaze or engobe, but rise to the surface by capillary attraction and so are unable to react properly with the ingredients below the surface.

Potash is usually added in the form of felspar or Cornish stone, but potassium nitrate (nitre) is sometimes used. Felspar adds the desired amount of flux in a more concentrated form than does Cornish stone, but if in excess it tends to cause peeling and may also cause crazing if the other constituents are not in the right proportions. Both felspar and Cornish stone also add alumina and silica to a glaze, and this must, if necessary, be corrected by reducing the proportion of clay or flint used.

Purdy [1] has found that a high proportion of felspar causes crazing in ware fired at Cones 1–3, but not in that fired at or above Cone 5. This is contradictory to Seger's observation. Purdy considers that with a clay : flint ratio of 3 : 3 to 3 : 7, felspar will not cause crazing unless more than 70 per cent. of felspar is present. If more than 35 per cent. of clay is present and the felspar is increased greatly, crazing may occur. As many pottery clays contain more than 35 per cent. clay, a high proportion of felspar generally causes crazing.

Where difficulties arise, due to the use of felspar, Cornish stone or a mixture of this stone and felspar may sometimes be satisfactorily substituted with advantage.

Soda is added in the form of a soda felspar or as a soluble salt, such as sodium carbonate, in which case fritting with some of the other constituents of the glaze is necessary. The action of soda is almost identical with potash and the two are often replaceable. Sometimes, soda produces a slightly more "fusible" glaze and potash a rather more glossy one.

The substitution of soda for lime, or the addition of soda to a glaze sufficiently rich in RO base, directly increases the tendency to crazing; it also increases the gloss and the fusibility of the earthenware glazes, but reduces their durability.

Glazes high in alkalies are generally suitable for bodies rich in quartz, whilst glazes low in alkalies are more suitable for bodies rich in alumina.

Lime is usually added as whiting or other form of a calcium carbonate, though calcium sulphate (plaster of Paris) is sometimes used. The addition of any lime compound increases the glossiness and fusibility of earthenware glazes and slightly reduces the tendency to crazing, but in terra-cotta glazes it tends to increase the amount of crazing; magnesia and barium oxide were even more deleterious in this

[1] *Trans. Amer. Cer. Soc.*, **13**, 157 (1911).

respect. Lime glazes usually require 0·5 equivalents of boric oxide to give the required fusibility to enable them to be used without other bases, but more than one equivalent tends to cause turbidity.

Mixtures of soda (or potash) and lime in glazes are very important and give better results than when either of these substances is used separately. The usual permissible range of composition of these two substances (expressed as oxides) is

$$\left.\begin{matrix}0{\cdot}6K_2O\\0{\cdot}4CaO\end{matrix}\right\} \text{ to } \left\{\begin{matrix}0{\cdot}2K_2O.\\0{\cdot}8CaO.\end{matrix}\right.$$

Soda may be partially or completely substituted for potash in the above proportions. Lime glazes usually require at least 4 equivalents of silica and at least 0·5 equivalents of alumina to give a satisfactory gloss.

Lead compounds are used in plumbiferous glazes and do not require any other flux, though others are often used to ensure greater stability. Insoluble lead compounds produce glazes which can be used at low temperatures without requiring to be fritted. They give great mobility and a high refractivity to glazes, and consequently impart a great lustre and brilliance unobtainable by any other element, although barium compounds sometimes give similar results in leadless glazes containing soda and boric acid. Small variations in the composition of leadless glazes are less important, and less likely to cause trouble than when no lead is present.

The chief disadvantage of lead compounds, and the reason for their restricted use, is the poisonous nature of soluble lead compounds. If lead compounds are fritted with silica, prior to use, their solubility is so greatly reduced as to render them practically harmless. The limit of solubility generally accepted is that suggested by T. E. Thorpe in evidence before the Lead Commission, viz. that in lead glazes the sum of the bases (including the alumina) in molecular parts, when calculated as lead monoxide, multiplied by 223 and divided by 60 times the sum of the acids, calculated as silica, should give a quotient which is less than 2, that is,

$$\frac{\text{Sum of bases (including alumina)} \times 223}{\text{Sum of acids} \times 60.} < 2$$

J. W. Mellor has pointed out that the multiplicands are unnecessary and that the same result is obtained more simply by requiring that the molecular ratio :

$$\frac{\text{Sum of bases (including alumina)}}{\text{Sum of acids}}$$

should be less than 0·5.

An alternative limitation, also suggested by Thorpe, is that not more than 1 per cent. of lead oxide should be capable of removal from a glaze by solution in dilute hydrochloric acid.

When fritting glaze materials containing lead, care should be taken not to frit any alkali or borax along with the lead compounds, or soluble substances may be formed which may cause poisoning. This objection may be overcome by using two kinds of frit—one containing all the lead and the other all the borax and soluble alkali compounds.

Boric acid and *boric oxide* are used in some glazes in place of part of the silica to lower the fusing-point without materially altering the constitution of the glaze. Its action is not thoroughly understood, some investigators regarding it as behaving like an acid, whilst others claim that it is basic in glazes. Thus, Seger, dealing with glazes in use in Germany, found that boric acid acts as an acid like silica. He states that it decreases the coefficient of expansion of glazes and decreases crazing, but Purdy and Fox,[1] and also Burt,[2] found that in glazes of the type used in the United States, boric acid increased the coefficient of expansion and also the crazing. Purdy and Fox have stated that boric acid and alumina both counteract devitrification, the best results being obtained with at least $0{\cdot}13B_2O_3$ to $1SiO_2$, irrespective of the oxygen ratio and alumina content, though the alumina content should not be less than 0·2 equivalents.

C. F. Binns [3] considers that boric oxide acts as a base in glazes, as he has found that glazes containing boron sesquioxide do not obey the bisilicate law if boron be regarded as acid, but do if the boron is regarded as basic. He considers that boric oxide should be classed with alumina in the molecular formula and that (apart from its effect on the fusibility) it may be used to replace alumina. This is confirmed by Singer,[4] who has also found that boric oxide and alumina may replace each other without altering any property of the glaze except the melting-point. He also found that either may be substituted by cobalt oxide in producing cobalt blue glazes, and that both change the colour of copper glazes in the same manner, though the intensity of boric oxide is nearly twice as great as that of alumina. Singer also found that boric oxide and other sesquioxides such as manganese, iron, cobalt, and vanadium can replace the alumina in zeolites, the series being amorphous.

The dual behaviour of boric oxide—sometimes as an acid and sometimes as a base—appears to be closely related to the general composition of the glaze. Thus, Stull and Radcliffe [5] found that when the base oxygen : acid oxygen ratio is less than 1 : 2, boric oxide behaves as an acid, but if this ratio is greater the boric oxide behaves as a base, whilst if the ratio is exactly 1 : 2, the boric oxide behaves as a free acid. When boric oxide behaves as an acid, it increases the tendency to crazing and when it behaves as a base it decreases the crazing.

Colouring oxides are added to glazes in order to produce certain desired colours. Such oxides may usually be included in the RO portion of a glaze formula and generally act as bases, though some sesquioxides, such as those of manganese, iron, cobalt, chromium, and vanadium are more appropriately included in the Al_2O_3 portion of a glaze formula.

The Adjustment of the Composition of Glazes and Engobes

It is impossible in this volume to deal exhaustively with the adjustment of glazes and engobes to enable them to fit any given ware or to overcome certain defects ; all

[1] *Loc. cit.* p. 385.
[2] *Trans. Amer. Cer. Soc.*, **7**, 131 (1905).
[3] *Ibid.*, **10**, 158 (1908).
[4] *Ibid.*, **12**, 676 (1910).
[5] *Ibid.*, **12**, 127 (1910).

that can be done here is to indicate some of the general principles involved. Further technical information on the subject will be found in the chapter on " Defects " in the author's *Clayworker's Handbook* (Griffin, London).

The chief purposes in altering the composition of an **engobe** are :

(i) To make it more fusible and thereby increase its adhesion and impermeability.

(ii) To increase its porosity.

(iii) To increase its shrinkage, so that it will better accommodate itself to the ware to which it is to be attached.

(iv) To reduce its shrinkage for the same reason.

(v) To alter its colour or to make it white.

The fusibility of an engobe may be increased by reducing the proportion of silica or clay or by increasing the proportion of potash, soda, or lime according to the composition of the engobe (p. 383). The porosity of an engobe may be increased by partly replacing a highly plastic clay by a less plastic one, by increasing the proportion of silica or grog, by substituting a coarser form of silica or grog for a finer one, or by adding a finely powdered organic substance, such as naphthalene, which will burn away in the kiln. The shrinkage of an engobe may be increased by adding more clay or by replacing a lean clay by a more plastic one ; it may be reduced by the reverse means or by adding silica, grog, or other non-plastic refractory material.

The colour of an engobe is altered by the addition of an appropriate metallic oxide (see p. 115), and an engobe may be made white by the use of purer material free from colouring impurities or by the addition of cobalt oxide (p. 113).

The chief purposes in altering the composition of a **glaze** are :

(i) To increase the fusibility and, therefore, its glossiness and transparency.

(ii) To increase the proportion of crystalline matter present and so produce a matte glaze.

(iii) To increase the shrinkage of the glaze and so prevent it from " peeling " off the ware.

(iv) To reduce the shrinkage of the glaze and so prevent " crazing " or the formation of hair-like cracks.

(v) To alter the colour of the glaze or to increase its opacity.

The **fusibility** of a glaze may be increased by

(*a*) Decreasing the proportion of silica and increasing the fluxes (bases), but preserving, as far as possible, a composition between a bisilicate and a trisilicate.

(*b*) Using a more powerful flux (base), but retaining the same molecular proportions.

(*c*) Increasing the number of fluxes, but retaining the same molecular proportions of base to silica.

(*d*) Decreasing the percentage of alumina and silica, but keeping the base : acid ratio within suitable limits.

(*e*) Increasing the proportion of boric acid with or without a reduction of the silica.

The **proportion of crystalline matter** in a glaze may be increased by replacing part of the present RO bases by zinc oxide, or, to a less extent, by reducing the

proportion of alumina in the glaze. Simple silicates crystallise far more readily than alumino-silicates.

The **shrinkage** of a glaze may be increased so as to prevent peeling and cracking by—

(*a*) Lowering the proportion of silica and increasing the fluxes without reducing the ratio of base to silica to less than that in a bisilicate.

(*b*) Increasing the proportion of silica at the expense of the boric acid (if present).

(*c*) Substituting a flux or base of high molecular weight for one of lower molecular weight.

(*d*) Adopting any of the methods used for increasing the fusibility of the glaze.

The shrinkage of a glaze may be reduced so as to prevent crazing by—

(*a*) Increasing the proportion of silica and decreasing the fluxes so as to form a bi- or trisilicate.

(*b*) Increasing the proportion of boric acid and decreasing the silica.

(*c*) Substituting a flux with a low molecular weight instead of one with a high molecular weight.

The **colour** of a glaze may be altered by the addition of a suitable metallic oxide (see *Colours*, p. 115), or it may be made whiter and more opaque by the addition of arsenic oxide, tin oxide, or cryolite, and by substituting materials which burn white for those which are coloured when burned.

Typical Glazes

The following are typical formulæ for glazes suitable for various purposes ; they are by no means exhaustive, as the number of different compositions which can be used for each purpose is enormous :—

Salt glaze is produced by throwing damp common salt into the kiln when its contents are at a sufficiently high temperature. The salt is decomposed by the heat and moisture forming soda (Na_2O) and hydrochloric acid (HCl). The former combines with the silica and alumina, of which the articles are made, forming complex silicates, the composition of which appears to vary considerably. According to Barringer, the limits of the alumina : silica ratio in the ware within which it is commercially possible to produce a good salt glaze are 1 : 4·6 to 1 : 12·5, and Mackler —who analysed pieces of glaze carefully chipped from the ware—found that salt glazes vary in composition from

$$1\text{–}2Na_2O\ Al_2O_3\ 3\cdot3\text{–}7\cdot5SiO_2,$$

the average being

$$1\cdot5Na_2O\ Al_2O_3\ 5SiO_2.$$

If an article is made of a highly aluminous clay deficient in free silica, it is usually very difficult to produce a good salt glaze on it, but the assumption that salt glazes are silicates and not alumino-silicates cannot be correct, as bricks made of pure silica do not form a good salt glaze when treated in the ordinary manner.

Terra-cotta glazes vary greatly in composition, as the clays used in the manufacture of terra-cotta vary so greatly. A glaze which has long been used with great success corresponds to the formula :

$$\left.\begin{matrix}0{\cdot}1\text{–}0{\cdot}7\mathrm{CaO}\\0{\cdot}5\text{–}0{\cdot}2\mathrm{K_2O}\\0{\cdot}4\text{–}0{\cdot}1\mathrm{ZnO}\end{matrix}\right\}0{\cdot}55\mathrm{Al_2O_3}\ 3{\cdot}3\mathrm{SiO_2}.$$

Stoneware consists of a vitrifiable body and can, therefore, be glazed at a higher temperature than most terra-cotta and faience ware. The composition of the glazes used naturally varies with the clays of which the articles are made. Thus, Seger has stated that the best stoneware glazes correspond to the formula :

$$\mathrm{RO}\ 0{\cdot}1\mathrm{Al_2O_3}\ 2{\cdot}5\mathrm{SiO_2},$$

whilst R. Purdy considers that a typical formula is :

$$\left.\begin{matrix}0{\cdot}3\text{–}0{\cdot}15\mathrm{CaO}\\0{\cdot}3\text{–}0{\cdot}45\mathrm{K_2O}\\0{\cdot}4\mathrm{ZnO}\end{matrix}\right\}0{\cdot}55\mathrm{Al_2O_3}\ 3{\cdot}0\mathrm{SiO_2},$$

and a Bristol stoneware glaze largely used by the author corresponds to :

$$\left.\begin{matrix}0{\cdot}18\mathrm{K_2O}\\0{\cdot}38\mathrm{CaO}\\0{\cdot}44\mathrm{ZnO}\end{matrix}\right\}0{\cdot}243\mathrm{Al_2O_3}\ 1{\cdot}58\mathrm{SiO_2}.$$

W. Scheffler has found that in transparent stoneware glazes for use under Cone 9, the silica should not exceed ten times the equivalent of the alumina or six times the actual weight of alumina and that at least 0·3 equivalents of potash should always be present, whatever the remaining 0·7 equivalents of bases may be.

Sanitary ware is largely made of fireclay covered with a felspathic engobe and a leadless glaze, which are fired at a temperature corresponding to Seger Cones 8 or 9 (1250° or 1280° C.). According to Parmelee and Williams,[1] the following requirements are important for fritted leadless glazes applied to sanitary ware :—

(*a*) The silica should be present to the extent of at least five equivalents.

(*b*) The alumina should be 0·5–0·6 equivalents in the absence of boric acid, but may sometimes be less if 0·5 equivalents of boric acid is present.

(*c*) The presence of 0·5 equivalents of boric acid is advantageous.

They found that a high proportion of lime caused dulness, a high proportion of zinc oxide caused blistering in the glaze, and a high proportion of alkali caused opalescence and crazing. In the best glazes they examined, the composition of the RO part of the glaze formula was :

$$0{\cdot}4\text{–}0{\cdot}6\mathrm{K_2O}\ 0\text{–}0{\cdot}3\mathrm{ZnO}\ 0{\cdot}4\text{–}0{\cdot}6\mathrm{CaO}.$$

An engobe and a glaze which may be regarded as the bases of most of those used

[1] *Trans. Amer. Cer. Soc.*, **18**, 812 (1916).

in this country for sanitary ware—the variations being largely due to local circumstances—correspond to the formulæ :

$$\textit{Engobe} \quad . \quad . \quad . \quad 1{\cdot}0K_2O\ 22Al_2O_3\ 65SiO_2.$$

$$\textit{Glaze} \quad . \quad . \quad . \quad \left\{\begin{matrix}0{\cdot}16K_2O\\0{\cdot}64CaO\\0{\cdot}20ZnO\end{matrix}\right\} 0{\cdot}22Al_2O_3\ 2{\cdot}5SiO_2.$$

It will be noted that this glaze does not conform to the conditions prescribed by Parmelee and Williams, yet it is extensively and satisfactorily used in this country, whilst glazes containing boric acid are seldom applied to sanitary ware.

Earthenware and Faience.—Seger gives the following relations between the RO, silica, and alumina in various glazes :—

Common earthenware and fine French faience $\left\{\begin{matrix}1RO \text{ to } 1{\cdot}5SiO_2\\1RO \text{ to } 3SiO_2.\end{matrix}\right.$

English and German white earthenware . $\left\{\begin{matrix}1RO\ 0{\cdot}01Al_2O_3\ 2{\cdot}5SiO_2\\1RO\ 0{\cdot}4Al_2O_3\ 4{\cdot}5SiO_2.\end{matrix}\right.$

According to E. Berdel [1] earthenware glazes free from lead and boric acid for temperatures between Cones 1 and 6 should have compositions within the following limits :—

$$\left.\begin{matrix}0{\cdot}3\left\{\begin{matrix}K_2O\\Na_2O\end{matrix}\right.\\0\text{–}0{\cdot}15ZnO\\0{\cdot}1\text{–}0{\cdot}2MgO\\0{\cdot}5BaO\end{matrix}\right\} 0{\cdot}14\text{–}0{\cdot}18Al_2O_3\ 1{\cdot}4\text{–}1{\cdot}8SiO_2.$$

A typical glaze for English earthenware (tableware) corresponds to—

$$\left.\begin{matrix}0{\cdot}29PbO\\0{\cdot}39CaO\\0{\cdot}10K_2O\\0{\cdot}21Na_2O\end{matrix}\right\} 0{\cdot}37Al_2O_3\left\{\begin{matrix}2{\cdot}62SiO_2\\0{\cdot}58B_2O_3.\end{matrix}\right.$$

As the terms " earthenware " and " faience " include many kinds of ware from those made of crude red-burning clay covered with a roughly-made glaze composed of galena and crushed quartz, flint, or fine sand, to some of the finest examples of the potter's art, no single formula can possibly prescribe the limits of composition of glazes and engobes for such a variety of wares.

Porcelains, like earthenware, vary greatly in composition and the glazes vary correspondingly. Seger has stated that the following are the maximum and minimum compositions for hard porcelain glazes :—

Maximum . . . $RO\ 1{\cdot}25Al_2O_3\ 12SiO_2$

Minimum . . . $RO\ 0{\cdot}5Al_2O_3\ 5SiO_2$

but he recommended that such glazes should be based on the composition of some

[1] *Ker. Rund.*, **25**, 88 (1917).

Seger cones, and Mellor [1] has suggested that the compositions shown below (which approximate to Cones 4–11) may be used as glazes for felspathic porcelain.

Cones Nos.	4–6	RO 0·4	Al_2O_3 3·5	SiO_2	Used as a glaze at Cone		7
		RO 0·5	„ 4·5	„	„	„	9
		RO 0·6	„ 5·5	„	„	„	10
„	7–8	RO 0·7	„ 6·5	„	„	„	11
		RO 0·8	„ 7·5	„	„	„	12
„	9–11	RO 0·9	„ 8·5	„	„	„	13
		RO 1·2	„ 11·0	„	„	„	16

Yaichiro Kitamura [2] gives the following formulæ for porcelain glazes to be fired at temperatures between 1380° C. and 1500° C. :—

At Cone 11	1·0RO(0·5KNaO 0·5CaO)	$0·9Al_2O_3$	$8SiO_2$
	1·0RO(0·1KNaO 0·9CaO)	$0·7Al_2O_3$	$5SiO_2$
At Cone 14	1·0RO(0·5KNaO 0·5CaO)	$1·05Al_2O_3$	$10SiO_2$
	1·0RO(0·1KNaO 0·9CaO)	$0·95Al_2O_3$	$9·5SiO_2$
At Cone 17	1·0RO(0·5KNaO 0·5CaO)	$1·1Al_2O_3$	$11·5SiO_2$
	1·0RO(0·1KNaO 0·9CaO)	$1·1Al_2O_3$	$14·5SiO_2$

Sortwell [3] has stated that the best porcelain glazes have an alumina-content of (0·3+$\frac{1}{12}$ silica), the silica varying from 3–13 equivalents, the permissible variation being greatest at the higher temperature. The proportion of alumina he recommends differs considerably from that used by European manufacturers of porcelain. Table CXVIII shows the percentage composition of various well-known porcelain glazes.

TABLE CXVIII.—*Chemical Composition of Glazes for Porcelain*

	Silica.	Alumina.	Ferric Oxide.	Lime.	Magnesia.	Potash.	Soda.	Loss on Ignition.	Formula.	Authority.
Pegmatite used at Sèvres .	70·64	16·87	0·73	1·31	0·20	4·22	4·97	0·34	RO 1·07R_2O_3 7·45SiO_2	M. Vogt.
Pegmatite used at Limoges .	76·11	14·61	0·66	1·44	0·42	2·99	3·03	1·23	RO R_2O_3 8·91SiO_2	Seger
Pegmatite used at Limoges .	75·99	14·80	0·37	1·09	0·36	4·31	3·49	0·65	RO 1·24R_2O_3 10·84SiO_2	„
Berlin glaze .	73·24	13·97	0·31	2·57	0·51	4·81	1·71	3·83	RO 1·12R_2O_3 9·58SiO_2	„
Japanese glaze*	61·97	12·92	0·39	9·57	tr.	4·17	1·12	10·21	RO 0·55R_2O_3 4·42SiO_2	„
Japanese glaze†	64·96	12·74	0·80	8·78	tr.	1·95	2·30	9·35	RO 0·59R_2O_3 5·04SiO_2	„
Chinese sea-green glaze ‡	64·80	14·33	1·39	10·09	1·55	5·61	0·81	1·39	RO 0·52R_2O_3 3·82SiO_2	„

* +0·30P_2O_5
† +0·16P_2O_5
‡ +Titanic acid
} included in Loss on Ignition.

[1] *Trans. Eng. Cer. Soc.*, **14**, 176 (1914–15). [2] *J. Chem. Ind.* (Japan), **24**, 89–105 (1921).
[3] *J. Amer. Cer. Soc.*, **4**, 718 (1921).

Coloured engobes and glazes are produced by (*a*) the suspension of a colouring oxide in the engobe or glaze, or (*b*) the formation of coloured compounds when the engobe or glaze is fired. Thus, copper oxide and silica in the presence of an alkali form a bright blue glaze, whilst the substitution of alumina or boric oxide for some of the silica produces a green colour. Cobalt-blue glazes are due to the production of cobalt zeolites, according to Singer ;[1] the replacement of half the cobalt by boric oxide or alumina intensifies the colour, boric oxide being most effective. Coloured glazes and engobes are chiefly produced by adding a suitable proportion of one or more of the following oxides to the glaze prior to applying it to the ware (see p. 115).

It is sometimes preferable to use specially prepared materials instead of the simple oxides ; for instance, what are known as *chrome-tin pinks* are prepared by calcining a mixture of a chromium compound, tin oxide, and a calcium compound so as to produce a colouring agent, which is added in suitable proportion to a clear glaze. Potassium bichromate is the most suitable chromium salt, a typical stain suggested by Seger consisting of—

Stannic oxide . . .	50 parts
Calcium carbonate . .	25 ,,
Flint	18 ,,
Borax	4 ,,
Potassium bichromate .	3 ,,

Prepared cobalt is made by heating hydrated black cobalt oxide to a white heat, after which it is cooled and finely ground. It should contain about 80 per cent. of cobalt and 20 per cent. of oxygen, and should be free from glassy or fused material, as this is an indication of the presence of impurities. The compositions of various other prepared colours also sold by firms dealing in potters' materials are regarded as trade secrets.

Opalescent glazes are produced by (*a*) using an excess of silica and a high oxygen ratio (at least 1 : 4). Purdy and Fox[2] found the best results in this case are obtained with 0·20 equivalent of alumina, an oxygen ratio of 4·5 and a $SiO_2 : B_2O_3$ ratio of 1 : 0·25. Whitmore,[3] however, prefers an oxygen ration of 1 : 5·5–6·5. He also suggests a $B_2O_3 : SiO_2$ ratio of not more than 1 : 3 or 1 : 4, 0·4–0·5 equivalents of lime and a firing temperature between Cones 1–5.

Purdy has recommended an opalescent glaze corresponding to—

(*a*)
$$\left.\begin{matrix}0{\cdot}126Na_2O\\0{\cdot}124K_2O\\0{\cdot}50CaO\\0{\cdot}250PbO\end{matrix}\right\}0{\cdot}2Al_2O_3\left\{\begin{matrix}2{\cdot}6182SiO_2\\0{\cdot}6546B_2O_3\end{matrix}\right.$$

(*b*) The precipitation of a silicate of boric oxide as suggested by Stull and Radcliffe.[4]

(*c*) Adding an opacifying agent which remains in suspension in the glaze, the most popular of these being tin oxide, arsenic oxide, magnesia, zinc oxide, and zirconia

[1] *Loc. cit.*, p. 389.
[2] *Loc. cit.*, p. 385.
[3] *Trans. Amer. Cer. Soc.*, **11**, 262 (1909).
[4] *Ibid.*, **12**, 129 (1910).

The proportion to be added depends largely on the nature of the glaze and the temperature at which it is fired. Five per cent. of tin oxide is usually ample.

Matte glazes are produced by (*a*) the precipitation or crystallisation of compounds from the molten glaze, *e.g.* calcium aluminate, calcium-aluminium silicates, or zinc silicates, the last being the easiest to produce (see *Crystalline Glazes*, p. 397); (*b*) the glaze being imperfectly fused during the firing process; (*c*) the formation of a crinkled skin due to the bulk of the glaze contracting more than the surface; (*d*) the elevation of the skin of the glaze by innumerable vesicles of gas; or (*e*) the addition of vanadium oxide, zinc oxide, or other crystallising agent to a glaze containing at least 0·15 equivalent of alumina. C. F. Binns [1] considers that matte glazes fired at a temperature corresponding to Cone 01 are best produced by using a mixture corresponding to—

$$RO\ 0{\cdot}35Al_2O_3\ 1{\cdot}6SiO_2.$$

He suggests that the best composition for the RO bases is $0{\cdot}09K_2O$, 0·20CaO, 0·575PbO, 0·135ZnO, but the following may also be used :—

(*a*).	(*b*).	(*c*).
0·225 K_2O	0·135 K_2O	0·200 CaO
0·575 PbO	0·170 CaO	0·575 PbO
0·200 ZnO	0·575 PbO	0·225 ZnO
	0·120 ZnO	

For higher temperatures (*e.g.* Cone 9), he suggests a mixture corresponding to—

$$\left.\begin{matrix}0{\cdot}3K_2O\\0{\cdot}7CaO\end{matrix}\right\}0{\cdot}64Al_2O_3\ 2{\cdot}4SiO_2.$$

According to E. Orton [2] matte glazes of type (*a*) may be produced at Cones 2–11 within the following range of composition :—

$$\left.\begin{matrix}0{\cdot}5\ -0{\cdot}1\ PbO\\0{\cdot}5\ -0{\cdot}1\ ZnO\\0{\cdot}1\ -0{\cdot}2\ K_2O\\0{\cdot}45–0{\cdot}35CaO\\0{\cdot}40–0{\cdot}30BaO\end{matrix}\right\}0{\cdot}2–0{\cdot}4Al_2O_3\ 1{\cdot}2–2{\cdot}4SiO_2.$$

When these glazes are overheated they produce bright, glossy glazes. Orton found that an excess of lead or of alkalies above the proportion mentioned produces a glassy structure, as also does an increase of silica, especially at high temperatures. According to Orton, variations in the proportion of alumina do not appear to affect

[1] *Trans. Amer. Cer. Soc.*, **5**, 50 (1903); **7**, 115 (1905).
[2] *Ibid.*, **10**, 547 (1908).

the mattness, but Sortwell [1] has found that aluminous matte glazes, maturing at Cones 12–16 and having an alumina : silica ratio of 1 : 4 for 3–6 equivalents of silica rising to 1 : 6 for 10 equivalents of silica, do not clear at higher temperatures, but are true matte glazes.

Crystalline glazes are most satisfactorily produced from glazes which are free from alumina, as this substance tends to prevent crystallisation, but if only 0·15 equivalent of alumina is present it may not interfere. Lime or zinc oxide appears to be essential for the production of good crystals. The chief oxides which give good crystals and may be regarded as *crystallising agents* are : zinc oxide,[2] titanium oxide, tungstic oxide, molybdic oxide, vanadic oxide, and bismuth oxide. Oxides of manganese, uranium, cobalt, iron, copper, and nickel may also be used for coloured glazes. According to Koerner,[3] bismuth oxide and uranium oxide produce crystalline glazes at as low a temperature as Cone 010–09, and tungstic oxide produces beautiful fernlike and star-shaped formations, showing partly iridescent reflexes quite unlike the effects obtained with zinc and titanium oxides.

Purdy and Krehbiel [4] found that manganese dioxide had the greatest tendency to cause crystallisation ; zinc oxide is next, but with it the crystals tend to segregate in local areas, leaving others devoid of crystals. If a fusible silicate (glaze) is coloured with a coloured silicate (as by adding cobalt) and is then saturated with zinc silicate whilst in the molten state, the zinc silicate will crystallise out as willemite and will be coloured by the coloured silicate, the background remaining colourless if there is no excess of colouring agent.

Titanic oxide produces very small crystals uniformly distributed through the glaze.

Although glazes with a 1 : 4 oxygen ratio are commonly used in the production of crystalline glazes, Purdy and Krehbiel consider an oxygen ratio of 1 : 2·8 to produce better and more uniform crystalline glazes. The lower oxygen ratio is confirmed by the researches of Schott on Jena glass.

Pukall [5] considers that the best crystalline glazes are obtained when copper and manganese oxides or mixtures of both of them are used, the best firing temperatures being at Cones 4–7. He obtained irregular results when using vanadic, molybdic and tungstic acids.

The composition of the " foundation glaze " from which crystalline glazes may be prepared by suitable additions is very important ; the following are typical formulæ for this kind of glaze :—

$$\text{To mature at Cone 09–2,}\quad \left.\begin{matrix}0{\cdot}1Na_2O\\0{\cdot}2CaO\\0{\cdot}7PbO\end{matrix}\right\}0{\cdot}05Al_2O_3\left\{\begin{matrix}2{\cdot}1SiO_2\\\\0{\cdot}2B_2O_3.\end{matrix}\right.$$

[1] *Loc. cit.*, p. 394.

[2] Zinc oxide differs from some other crystallising agents in producing silicate crystals instead of oxides.

[3] *Trans. Amer. Cer. Soc.*, **10**, 61 (1908).

[4] *Ibid.*, **9**, 319 (1907).

[5] *Ibid.*, **10**, 185 (1908).

To this is added 18–28 per cent. of a crystallising oxide (p. 397).

To mature at Cone 08–4, $\left.\begin{matrix}0{\cdot}25Na_2O\\0{\cdot}35K_2O\\0{\cdot}40CaO\end{matrix}\right\}0{\cdot}05Al_2O_3\left\{\begin{matrix}2{\cdot}0SiO_2\\\\0{\cdot}5B_2O_3.\end{matrix}\right.$

To this is added 2–25 per cent. of rutile or 0·25–2 per cent. of oxides of chromium, cobalt, or copper, or 5–10 per cent. of the oxides of iron, manganese, uranium, or nickel.

Purdy and Krehbiel [1] have found that the presence of soda is more conducive to the development of crystals than potash, the crystals in soda glazes being larger and grouped most pleasantly. They suggest that the best proportions of zinc to alkali are :

$$\left.\begin{matrix}0{\cdot}3ZnO\\0{\cdot}7KNaO\end{matrix}\right\}\text{ to }\left\{\begin{matrix}0{\cdot}6ZnO\\0{\cdot}4KNaO.\end{matrix}\right.$$

Aventurine Glazes.—The presence of finely-divided metallic particles in a glaze produces a spangled effect, resembling the mineral *aventurine*. Mackler [2] has used a glaze corresponding to—

$$\left.\begin{matrix}0{\cdot}25K_2O\\0{\cdot}25Na_2O\\0{\cdot}50CaO\end{matrix}\right\}\begin{matrix}2{\cdot}25SiO_2\\\\0{\cdot}75B_2O_3\end{matrix}$$

together with 20 per cent. of finely-divided metallic iron, and H. G. Schurecht [3] has found that red to black aventurine glazes may be produced with 0·41–0·81 equivalents of iron oxide in a glaze of the following composition :—

$$\begin{matrix}0{\cdot}4Na_2O\\\\0{\cdot}6PbO\end{matrix}\left\{\begin{matrix}0{\cdot}05Al_2O_3\\0{\cdot}25B_2O_3\\0{\cdot}41\text{–}0{\cdot}81Fe_2O_3\end{matrix}\right\}2{\cdot}4\text{–}4{\cdot}2SiO_2.$$

Glazes with $0{\cdot}41\text{–}0{\cdot}73Fe_2O_3$ give a red colour under oxidising conditions and a black one under reducing conditions. The ratio of iron oxide to silica is important, glazes containing $2{\cdot}4SiO_2$ requiring at least $0{\cdot}41Fe_2O_3$, and glazes containing $4{\cdot}2SiO_2$ requiring at least $0{\cdot}58Fe_2O_3$. Increases in the amount of iron oxide increased (*a*) the size of the crystals, (*b*) the number of crystals, (*c*) the refractoriness of the glaze.

Other metals, particularly copper and gold, may be used instead of iron. It is not necessary to employ the metals, as if the conditions of firing are suitable so that compounds are reduced to the metallic state, an aventurine effect will be produced. If the particles of metal are too small they will dissolve in the glaze and will merely colour it, producing a " stained glaze."

THE CHEMICAL COMPOSITION OF OTHER CERAMIC MATERIALS

Silica bricks should usually be made from rocks containing at least 97 per cent. of silica, as the best silica bricks have a chemical composition within the following limits :—

[1] *Loc. cit.*, p. 397. [2] *Tonind. Zeit.*, 207 (1890). [3] *J. Amer. Cer. Soc.*, 3, 971 (1920).

Silica	95–98 per cent.
Alumina	0·5–2·8 „
Iron oxide	0·3–1·3 „
Lime	0·2–2·4 „
Soda and potash	0·2–1·5 „

If the impurity in silica rocks is in the form of clay, as in a ganister, a silica percentage of only 90 may not be harmful, but where the impurities are fluxing oxides, such a large proportion would be very detrimental to the refractoriness of the goods made from it.

There is no serious difficulty in obtaining silica rocks which contain less than 4 per cent. of clayey matter and 1 per cent. of fluxes ; some silica rocks contain as much as 99 per cent. of silica and less than 1 per cent. of impurities.

The chemical composition is not, in itself, a reliable guide, as some of the purest quartzites are often unsuitable for physical reasons, as shown on p. 14. At the same time, it is desirable to use a material which is as pure as possible, consistent with the requisite physical structure. The relative values of wholly crystalline and bonded quartzites have been considered on p. 18.

A good quartzite should contain about 97·5 per cent. of silica, 1·5 per cent. of alumina, and not more than 0·5 per cent. of iron oxide. The proportion of alumina and iron oxide together should not exceed 2 per cent. The proportion of alkalies should not exceed 2 per cent., nor the total fluxes more than 3 per cent. Alumina in the form of clay may be present up to about 2 per cent., but the total lime and alumina should be not more than about 4 per cent.

The alumina in quartzites is generally combined in the form of felspars, micas, or alumino-silicates such as kaolinite. The presence of a lower percentage of combined water, together with a high percentage of alumina and potash, indicates the presence of potash felspar, whilst larger proportions of water and potash indicate mica, and low potash and high alumina and water indicate kaolinite or clay. Potash occurs in silica rocks in the form of felspar or mica, an excess of water indicating the presence of the latter compound. The lime in silica rocks may be combined either as calcite, dolomite, soda-lime, felspar, or as calcium phosphate. Lime is also added artificially to give the necessary bonding strength to the bricks. As a rule, about 2 per cent. is used. Other basic fluxes used as bonds are (*a*) Portland cement ; (*b*) soda compounds, including water-glass ; (*c*) ammonium alum ; (*d*) calcium chloride ; (*e*) magnesia ; (*f*) felspar or Cornish stone ; (*g*) complex silicates ; (*h*) barium sulphate ; and (*i*) calcium sulphate. Carbon dioxide is sometimes present in silica rocks as a result of the presence of lime or magnesia or both, in the form of carbonates or in the form of chalybite, the latter being very important. Combined water in silica rocks may indicate the presence of several minerals, including mica, clay, and limonite. Usually it varies from 0·1–1·0 per cent., though in exceptional cases it may be as high as 3·5 per cent. As a general rule, not more than 5 per cent. of metallic oxides other than alumina should be present in silica rocks, which are to be bonded with lime, or they will be too impure to be used as first-class refractory materials.

The ganister employed in the manufacture of ganister bricks usually contains 87–96 per cent. of silica, 4–5 per cent. of alumina, 0–1·5 per cent. of ferric oxide, 0·25–0·75 per cent. of lime and magnesia, and 0–1 per cent. of alkalies. The best qualities of Yorkshire ganister contain about 95 per cent. of silica.

The bricks termed in America " quartzite " bricks are not the same as those so named in this country, but consist of natural mixtures of fireclay and silica containing 70–80 per cent. of silica ; they correspond more nearly to what, in this country, are known as " semi-silica " bricks.

The Institution of Gas Engineers terms materials containing over 92 per cent. of silica, *silica material*, and those containing 80–92 per cent. of silica, *siliceous material.*

The American Gas Institute specifies that silica bricks and blocks should be made from material containing over 94 per cent. of silica, not more than 1·7 per cent. of iron oxide, and between 1·7 and 3 per cent. of lime.

Further analyses of siliceous rocks will be found in the author's *Refractory Materials: Their Manufacture and Uses* (Griffin), and *Sands and Crushed Rocks* (Frowde, Hodder & Stoughton).

Refractory silica sands to be used for lining furnaces and for furnace hearths should contain 95–99 per cent. of silica when used in steel furnaces, whilst for lower temperatures, such as are attained in copper furnaces, a lower percentage of silica may be permitted. In America, copper converters have been used satisfactorily when lined with a mixture containing only 60–70 per cent. of silica. For the highest temperatures not more than 0·5 per cent. each of iron oxide, lime, magnesia, and alkalies should be present in the sand, whilst for lower temperatures rather less pure sands may be employed. For further information see the author's *Sands and Crushed Rocks* (Frowde, Hodder & Stoughton, London).

Silica glass (also known as **fused quartz, fused silica, vitreosil,** etc.) should consist, as nearly as possible, of pure silica, the presence of impurities reducing the refractoriness and resistance to corrosion of the articles and spoiling their appearance. For transparent silica ware, not more than 0·3 per cent. of impurities is allowable, and opaque silica ware is made from sands containing at least 99 per cent. of silica and as little iron oxide as possible. See also the author's *Sands and Crushed Rocks* (Frowde, Hodder & Stoughton, London).

Spinels correspond to metallic aluminates (p. 356), the mineral spinel ($MgO.Al_2O_3$) showing on analysis 28 per cent. of magnesia and 72 per cent. of alumina. Various artificially prepared spinels, corresponding approximately to the formula $ROAl_2O_3$ have been proposed as refractory materials, but have not been used extensively—chiefly on account of their cost. The chief metallic oxides forming the RO in the above general formula are those of iron, magnesium, sodium, chromium, zinc and copper.

Engelhorn [1] has stated that spinels containing magnesia and zinc are the most resistant to alkalies, whilst those containing magnesia and chromium oxide are the most resistant to lime, cement, alkali-fluxes, glasses, etc.

[1] *Eng. Pat.*, 16,714 (1906).

Magnesite and Magnesia Bricks.—The best magnesites contain over 45 per cent. and often 47·5 per cent. of magnesium oxide. The proportion of lime varies from 0–5 per cent., and the iron oxide and alumina together sometimes reach 12 per cent. in Styrian magnesite ; the Grecian and Indian magnesites are much purer.

Iron oxide is not regarded as an objectionable impurity, as it appears to act as a catalytic agent which facilitates the dissociation of the magnesite and effects the formation of periclase at a lower temperature than is possible with a pure magnesite ; for this reason 2–4 per cent. of it is regarded as a useful constituent. Magnesites containing a small proportion of iron oxide are preferred by manufacturers of magnesite bricks to the purest varieties, as the former can more readily be converted into dead-burned magnesia.

The effect of silica on magnesite is to lower its refractoriness, as the magnesian silicate which is formed when the magnesite is heated is more fusible than either the magnesia or the silica. A small proportion of silica is not very objectionable as, when fused, it forms a good bond. In fact, S. G. Thomas considered the presence of at least 5 per cent. of silica to be necessary for this purpose, and patented the addition of clay to make up this amount if it was lacking. He found it was undesirable, however, to increase the amount of alumina present by using too much clay.

For refractory purposes the following are the maximum proportions of fluxing oxides usually regarded as allowable in magnesite :—

Lime	5 per cent.
Alumina	5 ,,
Silica	5 ,,
Iron oxide	8 ,,
Alkalies	3 ,,

Dead-burned magnesia of the best quality should not contain more than half these proportions of impurities, with the possible exception of the iron oxide.

Magnesia bricks vary considerably in chemical composition according to the nature of the materials used in their manufacture. Bricks made from Styrian magnesite usually contain about 85 per cent. of magnesia, 1 per cent. of alumina, 8 per cent. of iron oxide, 5 per cent. of silica, and 1 per cent. of other impurities. Bricks made from Greek magnesite contain usually 92 per cent. or more of magnesia, about 2 per cent. of alumina, practically no iron oxide, 1–5 per cent. of silica, and up to 1 per cent. of lime. For the reasons mentioned above, however, many bricks made from Grecian magnesite have about 6 per cent. of iron oxide purposely added. See also the author's *Refractory Materials : Their Manufacture and Uses* (Griffin).

According to Kowalke and Hongen [1] the addition of aluminium, chromium, titanium, and zirconium oxides, and especially silica, increases the strength of magnesia bricks at high temperatures. By the addition of 7·5 per cent. of silica the refractoriness under load was, in one case, increased from 1680°–1870° C.

[1] *Trans. Amer. Electrochem. Soc.*, **33**, 215 (1918).

Dolomite and Dolomite Bricks.—Pure dolomite has a composition corresponding to the formula $CaCO_3MgCO_3$ or $CaMgC_2O_6$, but natural dolomites and magnesian limestones usually contain varying proportions of calcium and magnesian carbonates on account of the presence of an excess of one or other of these materials ; they are, in fact, mixtures rather than compounds, though rocks consisting almost wholly of pure dolomite are abundant in some parts of the world.

The pure double carbonate of lime and magnesia contains 21·75 per cent. of magnesia, 30·5 per cent. of lime, and 47·75 per cent. of carbon dioxides, but the dolomites generally used contain about 28–35 per cent. of lime, 14–20 per cent. of magnesia, 1–7 per cent. of silica, 0–14 per cent. of alumina, 0·5–5 per cent. of ferric oxide, and 43–46 per cent. of carbon dioxide.

S. G. Thomas gives the following average composition of suitable dolomites for refractory purposes :—

Lime	about	33 per cent.
Magnesia . . .	18–20	,,
Carbon dioxide . .	42–46	,,
Silica	less than 7	,,
Iron oxide and alumina	,, 5	,,

Dolomite containing a small amount of alumina and ferric oxide is often preferred to the purer varieties, as it enables the dolomite to be " dead-burned " more readily. In some cases, iron oxide or " iron scale " is added artificially for the same purpose. As much as 20–30 per cent. of iron oxide may be added without reducing the refractoriness of the mixture to below Cone 31. Such large additions are, however, unnecessary and undesirable.

Dolomite bricks have a composition similar to that of the calcined materials, with the addition of a small quantity of clay added for bonding purposes. For further information see the author's *Refractory Materials* : *Their Manufacture and Uses* (Griffin).

Pure calcareous limestone is scarcely used as a refractory material, but lime is an important base in the manufacture of glass and *whiting* (finely ground calcium carbonate) is an important ingredient in some glazes. *Chalk* is used in the manufacture of some bricks and pottery. For further information see the author's *Refractory Materials* : *Their Manufacture and Uses* (Griffin).

Bauxite and Bauxite Bricks.—Pure alumina is seldom used for the manufacture of bauxite bricks and other refractory articles. The bauxite usually employed for this purpose contain about 90 per cent. of alumina, though much less pure bauxites are used, some containing as little as 40 per cent. of alumina. Diaspore (which shrinks less than bauxite when heated) has recently been used instead of bauxite for aluminous bricks.

The principal impurities in bauxites, as shown by analysis, are : silica, iron oxide, titanic oxide, manganese oxide, vanadic oxide, lime, magnesia, alkalies, sulphur trioxide, and phosphoric acid.

Very small proportions of impurities seriously affect the refractoriness of bauxites,

so that for refractory purposes the finest materials should be employed, the following being regarded as the permissible limits of composition :—

Alumina . . .	50–90 per cent.
Silica	3–25 ,,
Iron oxide . . .	0·5–12 ,,
Water	10–30 ,,
Other impurities . .	less than 8 ,,

Red bauxites contain a considerable amount of iron oxide, which appears in some way to be chemically combined with the alumina and not merely mixed with it. This iron oxide greatly reduces the refractoriness of the bauxite and so renders it of small value as a ceramic material.

The proportion of water in bauxites is not always constant ; some bauxites possess marked colloidal properties, and so may contain very variable amounts of water.

As pure bauxite is devoid of plasticity, it must be mixed with a suitable binding agent, fireclay or china clay being usually employed. Unfortunately, a large proportion of clay is usually necessary, and this seriously detracts from the quality of the product. Bauxite bricks which contain more than 15 per cent. of silica are scarcely superior to fireclay bricks, and the latter are much cheaper. The best bauxite bricks have a molecular silica : alumina ratio of 1·47, though in some cases good bricks can be made with a ratio of 1 : 3·5.

For further information see the author's *Refractory Materials* : *Their Manufacture and Uses* (Griffin).

Fused Alumina.—The bauxites used for making fused alumina should not contain more than 6–7 per cent. of silica or the product will be deficient in refractoriness and, consequently, it would not be worth the cost of fusing. The proportion of iron oxide present is less important, as it can be reduced to metallic iron during the fusing process and so separated from the alumina.

According to F. Engelhorn, the addition of magnesia and zinc oxides to alumina prior to fusion increases its resistance to alkalies, whilst chromium oxide and magnesia increase its resistance to lime, cement, and glass.

Zirconia, Zircon and Zirconia Bricks.—The zirconia ore of São Paulo contains varying proportions of zirconium oxide, the best rock in the form of black glassy pieces being almost pure zirconia, whilst the pebbles contain 90–93 per cent. zirconia. A grey or bluish-black ore contains zirconia and zircon or zirconium silicate and has the equivalent of 70–85 per cent. zirconia. These ores can be purified and a material containing 99·5 per cent. of zirconia obtained. The Ceylonese baddeleyite contains up to 99 per cent. of zirconia. Pure zircon contains about 67 per cent. of zirconia and 33 per cent. of silica. Zircon sand usually contains about 64 per cent. of zirconia, together with some iron oxide as an impurity.

Zirconia bricks have a similar composition to the raw materials from which they are made, the bond being usually organic, so that it burns away during the firing, though sometimes fireclay is used as a bond. Several attempts have been made to use highly purified zirconia for the manufacture of bricks, but the cost is usually

regarded as prohibitive. See also the author's *Refractory Materials*: *Their Manufacture and Uses* (Griffin).

Chromite and Chromite Bricks.—Chromite used for the manufacture of chromite bricks should contain at least 40 per cent. of chromic oxide, but some ores are used which contain only 35 per cent. Silica is undesirable, and not more than 6 per cent. should be present. The presence of clay in chromite is not harmful in proportions up to 20 per cent. Simonis has found that a chromite containing 10 per cent. of kaolin had a refractoriness corresponding to Cone 41, whilst one containing 20 per cent. of kaolin had a refractoriness corresponding to Cone 35. The latter is the minimum refractoriness usually allowable for chromite bricks. Larger proportions of clay cause the refractoriness to be rapidly reduced, 70 per cent. of clay reducing the refractoriness to Cone 17. Table CXIX shows the amount of chromic oxide in various chromite ores.

TABLE CXIX.—*Composition of Chromite*

Source.	Per cent. Chromic Oxide.	Source.	Per cent. Chromic Oxide.
Quebec . . .	20–50	Khanozai, Baluchistan.	54
S. Rhodesia . .	42–51	Mysore . . .	up to 52
Transvaal . . .	35–45	Brusa, Asia Minor .	50

Chromite bricks generally contain 33–36 per cent. of chromic oxide, though the best qualities may contain up to 65 per cent.

Carbon Bricks and Crucibles.—Carbon is used in the form of coke and of graphite. Bricks made of coke and tar usually contain 7–14 per cent. of ash. Larger proportions are undesirable as it decreases the refractoriness of the bricks.

The graphite or plumbago used for crucibles varies greatly in composition. Some varieties, such as the best Ceylon graphites, contain 99 per cent. of fused carbon, whilst others may only contain 60–70 per cent. The best qualities should usually have over 85 per cent. of fused carbon. Some graphites contain a notable proportion of volatile matter (sometimes as much as 10 per cent.), whilst the amount of ash varies up to 30 per cent. The best graphites are those which are as low as possible in ash and volatile matter. Thus, the best quality of Ceylon graphite contains only 1 per cent. of ash.

Carbide and Carboxide Bricks, etc.—The best-known carbide used in the ceramic industries is *carborundum*, which usually contains about 65 per cent. of silica, 30 per cent. of carbon, and 5 per cent. of various impurities. Similar materials are sold under various trade names, such as crystolon, silfrax, silit, silundum, siloxicon, and fibrox.

Carbide bricks, crucibles, etc., consist of carborundum or similar material bonded

with clay, water-glass, lime, Portland cement, or a temporary bond such as mineral oil, tar resin, or glycerin.

Table CXX shows the analyses of various kinds of carborundum.

TABLE CXX.—*Analyses of Carborundum*

	Theoretical Composition.	Moissan's Pure Product.	Commercial Carborundum.	Purified Carborundum.	Amorphous Silicon Carbide.
Silica . . .	70	69·93	62·70	69·10	65·42
Carbon . .	30	29·90	32·26	30·20	27·93
Alumina and Ferric oxide	..	..	0·93	0·46	5·09
Lime . . .	..	..	..	0·15	0·38
Magnesia . .	..	..	0·11	..	0·21

Further particulars concerning carbides will be found on p. 357 and in the author's *Refractory Materials: Their Manufacture and Uses* (Griffin, London).

CHAPTER X

THE MINERALOGICAL COMPOSITION OF CERAMIC MATERIALS

To describe fully all the mineral forms occurring in both raw and fired ceramic materials would occupy a very large volume, as they are so diverse and complex; hence, it is only possible to indicate briefly their chief characteristics and those of the more important forms produced during the firing or burning of some of the materials. A very large number of minerals occurring in clays and other ceramic materials are present in such exceedingly small proportions, that under most circumstances their existence may be ignored, and it is only when they are present in abnormal proportions, or when a material is to be used for some special purpose, that some of them become important.

The mineralogical composition of clays and other ceramic materials may be determined in several ways, the most convenient of which are :

(*a*) A microscopical examination—preferably following the preliminary separation of the minerals into various groups by means of mechanical methods of separation.

(*b*) Rational analysis.

(*c*) By calculating the results of an ultimate chemical analysis.

Methods (*b*) and (*c*) are indirect and give only approximate results, unless the nature and number of the various minerals present is accurately known.

The microscopical examination of a clay or other ceramic material may be made by various methods according as the material viewed through the microscope is—

(*a*) In the form of a powder, the particles of which are scattered on a glass slide and illuminated by light passing upwards through the particles into the microscope (transmitted light), or by directing a beam of light down upon them (reflected light). In the former case, the light may be either normal or polarised. By means of normal light, the transparency or opacity, and the shape, colour, and distribution of the individual particles may be seen; but isotropic minerals are less visible in polarised light, and by its use some minerals are seen to have special optical properties which enable these minerals to be distinguished from others.

(*b*) A fractured surface of a block of the material; this must be examined by reflected light.

(*c*) A polished surface of a block of the material; this is examined by reflected light.

(*d*) A very thin section of the material, obtained by grinding a sample until it is

about $\frac{1}{1000}$ inch thick and is sufficiently transparent when mounted in Canada balsam for its structure to be examined either by transmitted or reflected light.

The principal features which may be examined under the microscope are the structure of the material (Chapter I), the size and shape of the individual grains (Chapter II), and—in a thin section—the proportion of each may be roughly estimated. Other properties which may be examined by the aid of the microscope in order to identify various mineral forms are the cleavage, alteration products, refractive index, pleochroism, birefringence, extinction angle, interference figures, twinning of crystals, etc. Some of the notable properties are mentioned in connection with the mineral forms in the following pages and also in Chapter XV, whilst still more detailed information will be found in works dealing particularly with Mineralogy and Petrology.

The study of the microscopical structure of fired ceramic and other refractory materials is often useful for ascertaining the extent to which they have been changed by the heat. In some cases, a new crystalline form will be produced, as when clay is converted into sillimanite (p. 413), quartz into cristobalite or tridymite (p. 426), and magnesite into periclase (p. 427), but even where less extensive changes occur they often may be recognised by means of the microscope. Thus, if the firing of a piece of clay-ware or of a silica brick has been effected at a relatively low temperature, the edges of the grains will still be sharp, as the heating has not been sufficient for much solvent action to occur ; but if the material has been fired at a higher temperature, the grains which were previously " sharp " will usually be found to be more or less corroded and rounded by the solvent action of the fluxes and by the fused glassy matrix, and, in some cases, a large part of the original material may have been dissolved and afterwards recrystallised in some other form.

For many purposes, an examination of the powder with a powerful lens or under a low-power microscope is sufficient, as a magnification of 20 diameters will show all that is necessary, but for an exhaustive examination a first-class petrological microscope is required.

Preparation of Samples.—If the material to be examined is in the form of a block, it may be prepared for examination by grinding or polishing an existing surface, or it may be broken, sawn, or chipped, and the fractured surface may be either ground and polished or examined in its natural state. If the sample is to be examined as a transparency it must be ground sufficiently thin (*supra*).

In order more easily to discriminate some of the constituents, various etching and staining liquids may be applied for a limited time to the upper surface of the section. The various methods of etching are described in the standard works on Mineralogy and Petrology.

Such detailed work as the cutting and polishing of samples and the preparation and mounting of transparent sections is generally best undertaken by an expert, who is able to do this work more expeditiously than can anyone who is not used to such delicate manipulation.

When *powdered materials* are to be examined under the microscope, it is usually desirable to subdivide the material by one or more of the following mechanical means of separation so as to facilitate examination. Unless this is done, small crystals may

be obscured by the greater volume of apparently amorphous matter and their presence not recognised.

The methods of separation usually employed for this purpose are :—

(*a*) *Sieving.*—If the powder is passed through a series of sieves of different mesh so as to separate the grains of different sizes, the examination is facilitated. The material may be sieved in the dry state or with the aid of water, the latter being preferable when much clay or fine dust is present. By this means much of the sand and other non-plastic material may be separated from the clay (see *Mechanical Analysis*, p. 44), and in the case of natural powders, such as sands, it will be found that most of the grains of high specific gravity will segregate in the fine portions, whilst the quartz and " lighter " minerals are retained on the sieves. When sieves are used, all the different portions into which the material is divided should be examined separately. Some writers on petrology suggest that the finest particles should be washed away by the aid of water, but if the sample under examination consists of clay, the portion so removed by the water should be collected and examined separately.

Instead of sieves, an elutriator (p. 50) may be employed, though little can usually be learned from a microscopical examination of the finer grades separated by elutriation or sedimentation (p. 53).

(*b*) *Use of Heavy Liquids.*—When a material consists of particles of different specific gravities, they may be separated by dropping them into various heavy liquids. Bromoform, with a specific gravity of 2·85, is very convenient, as clay and quartz float in it, but the heavy detrital minerals sink and so are easily separated, and their microscopical examination is made much easier. Various other solutions may be used if necessary with specific gravities up to 3·5, whilst molten salts may be employed for specific gravities up to 5·3, but their use is difficult and troublesome to those who have not had a special training in this work. Further details will be found in the author's *Sands and Crushed Rocks* (2 vols., Frowde, Hodder & Stoughton) and in standard works on Mineralogy and Petrology.

(*c*) *Diffusion columns* are sometimes used when a mineral consists of a considerable number of different compounds. A diffusion column is made by placing two miscible liquids of different specific gravity in a tall glass cylinder, the lighter liquid being carefully placed on the heavier one so as to avoid mechanical mixture. In the course of time, the two liquids will diffuse into each other, producing a column of liquid the specific gravity of which increases progressively with the distance from the air-liquid surface. If a mixture of particles of different specific gravities is dropped carefully into such a column the light particles will float on or near the top, whilst the heavier particles will sink to various depths and the heaviest ones will sink to the bottom of the vessel. If particles of known specific gravity (which act as guides) are dropped into the column, the nature of the various minerals in the sample may be, to some extent, determined by comparing their positions with those of the " guides." The limitations of diffusion columns are obvious and it is usually better to employ a series of liquids of known specific gravities, as much sharper separations may then be effected.

(*d*) *Magnetic separation* may be used to separate some minerals from others having different magnetic properties (Chapter XIV). Thus, the more highly magnetic grains may be removed by applying a permanent magnet to the powder, and the lesser magnetic grains may afterwards be removed by means of an electromagnet. If the poles of the magnet are adjustable so as to place them at any desired distance apart, magnetic fields of varying intensities may be produced so as to attract minerals of varying susceptibilities and so facilitate their removal. Further information will be found in Chapter XIV. Magnetic separation is used on a large scale, but when examining a sample in the laboratory, quite small appliances may be employed.

(*e*) *Electrostatic separation* is sometimes convenient, and is dependant upon the electrical conductivity of the minerals present. The separation of minerals by this means is described in Chapter XIV.

Rational Analysis.—A method which was, at one time, regarded as showing the mineralogical composition of certain materials (especially clays) is that known as *rational analysis*—a term proposed by Seger, who hoped that it would enable complex mixtures such as natural clays to be subdivided into their various mineral constituents, and by this means show what could not be ascertained from an ultimate chemical analysis, but in this respect the process does not fulfil expectations. A so-called " rational analysis " is made by boiling a known weight of the material with concentrated sulphuric acid for several hours, after which the liquid is cooled, diluted with water, and filtered ; the residue is boiled with a solution of sodium carbonate or hydrate to dissolve any free amorphous silica derived from the clay, and is again filtered, washed, dried, and weighed. It consists chiefly of quartz, felspar, mica, and analogous materials.

The clay is presumed to be decomposed into aluminium sulphate and free silica, both in a soluble state. Both the residue and solution may be analysed and the proportion of silica, alumina, magnesia, lime, soda, and potash in each determined, and from the figures so obtained the proportion of clay, quartz, felspar, mica, etc., estimated.

Unfortunately, there are many serious objections to the rational method of analysis which prevent accurate results being obtained and limit its usefulness. Some clays are not entirely decomposed by sulphuric acid, and the products of its decomposition are not always entirely removed from the residue, thus causing an appreciable error. Other minerals besides clay are dissolved more or less completely by sulphuric acid, so that the reported proportion of clay will be higher than it should be. Felspar, hornblende, augite, biotite, andalusite, epidote, glauconite, and muscovite are all attacked to a variable extent by sulphuric acid, and a corresponding amount of any or all of these materials may be reported as clay. Largenbeck has shown that as much as 20 per cent. of the felspar may be dissolved in a rational analysis and most of any mica dust present is decomposed and dissolved. The smaller the particles of impurities present, the more serious is the error due to undue solution in sulphuric acid. The concentration of the acid, the duration of the heating, and the size of the particles, all affect the results and lead to errors, and although various modifications of the method have been proposed, there are none of them wholly satisfactory.

For these reasons, a rational analysis is seldom of much value, though it is sometimes useful in investigating variations in the composition of a bed of clay for the purposes of work's control or for investigations where it is used in conjunction with other evidence.

Most of the objections to this process are due to the term " rational analysis." If this had never been used, but the results had been described as " solubility in sulphuric acid," many erroneous conclusions respecting the composition of clays would have been avoided.

Another method of partial analysis for determining the true clay in a natural clay consists in calcining the material at 730°–750° C. and then determining the amount of alumina soluble in hydrochloric acid and of silica soluble in caustic soda. The clay is decomposed on calcination, without the quartz, felspar, and mica being affected. It may be necessary to correct the result to allow for the presence of limestone or of other minerals which, after calcination, yield alumina and silica in soluble form (pp. 412, 413), but usually such minerals are absent.

The results are still more accurate, in the case of impure clays, if " sand " has previously been separated by washing the sample through a 200-mesh sieve.

Recalculated Analysis.—If the whole of the minerals present in a material are known and they are not too numerous, or if, without serious error, a number of similar minerals can be regarded as " felspar " or " mica," or similar type minerals, an approximate idea of the mineralogical composition of a clay or other ceramic material may be obtained by recalculating the results of an ultimate chemical analysis. If a mixture is known to consist wholly of pure clay, felspar of known composition, and pure quartz, a recalculation of the results of a chemical analysis will give wholly accurate results. In most cases, however, various errors are introduced owing to assumptions which are made with regard to the composition of the felspar, quartz, and clay.

In a clay devoid of carbonates and soluble salts it is customary to assume that all potash, soda, lime, and magnesia are present as " felspar," each molecule of these oxides being assumed to combine with one molecule of alumina and six molecules of silica. The equivalent amounts of alumina and silica are deducted from the totals of these oxides found by analysis. Each surplus molecule of alumina is then assumed to combine with two molecules of silica and two of water forming " clay," and any surplus silica remaining after deducting that assumed to be present as clay is regarded as " quartz." Hence, the composition of a natural clay may be reported in terms of " felspar," " clay," and " quartz." Iron compounds create a difficulty, the serious nature of which is usually shirked by assuming that they are present as ferric oxide.

The most serious errors caused by such methods of recalculation occur when a clay or similar material does not contain felspar, but other silicates or aluminosilicates. Thus, commercial Cornish china clay contains a considerable proportion of muscovite (mica), but is almost devoid of felspar. Its mineralogical composition may be expressed with a fair degree of accuracy if the results of a chemical analysis are recalculated in terms of " clay," " mica," and " quartz."

If care is taken to ascertain by a microscopical examination or by other means the nature of the minerals present, a recalculation of a chemical analysis often yields

results of great practical value, even when they are not wholly accurate. The errors in the case of natural clays may often be reduced if, prior to chemical analysis, the material is subjected to a mechanical analysis (p. 44) in order to remove coarse particles of sand, etc., the chemical analysis being confined, if necessary, to the " clay portion."

MINERALOGICAL COMPOSITION OF CERAMIC MATERIALS

The principal minerals in the ceramic industries may be arranged in the following groups : (*a*) *clays* and analogous materials, with the minerals occurring as impurities in them ; (*b*) minerals composed almost wholly of *free silica* ; (*c*) minerals composed chiefly of *alumina* ; (*d*) *magnesite* and allied minerals ; (*e*) *limestone* ; (*f*) *dolomite* ; (*g*) *zirconia* and allied minerals ; (*h*) *titanium* minerals ; (*i*) *chromite* and allied ores ; (*j*) *graphite* and other forms of carbon ; and (*k*) *carbides.*

In each case, it is convenient to describe associated minerals in connection with the chief mineral in each group, but it should be remembered that almost any of the minerals mentioned may occur in any group.

Mineralogical Composition of Clays

Clays, unless specially purified, are complex mixtures of many minerals and, as explained on p. 343, the precise nature of " true clay " is by no means fully understood. Most clays consist of a heterogeneous mixture of one or more alumino-silicic acids resembling kaolinite, with other minerals, which may conveniently be regarded as sand or silt, and sometimes with limestone dust. When these coarser particles are separated the residuum bears some resemblance to china clay and to kaolinite, though in the case of some highly plastic and very impure clays the purest " clay " obtainable is still obviously very impure.

As the nature of raw clay has already been described on p. 343, it is sufficient here to mention briefly some of the characteristics of the mineral kaolinite and some other minerals analogous to clay and the various minerals which may be regarded as " impurities " in clay.

China clay when carefully purified appears to be for the most part amorphous, but it has recently been found by X-ray examination (p. 19) to be extremely minutely crystalline. When viewed through a sufficiently powerful microscope it is found to contain numerous crystalline particles, which appear to be kaolinite, some of these crystals having the form of a pile of discs, one on top of another (known as *rouleaux*), or have a fan-shaped arrangement (known as *vermicules*). The crystals have a pearly lustre by reflected light, and have an index of refraction of 1·55–1·56 and a lower birefringence than mica, with which they may be confused. They sometimes show good polarisation colours, though generally they are extinguished parallel to the basal plane without showing any colour. A biaxial interference figure is shown by basal flakes which extinguish parallel to the *a* axis.

It is not wholly satisfactory to assume that the apparently amorphous matter and the crystals are identical minerals, though this appears to be the case. The

possibility of other alumino-silicic acids of a similar composition must not, however, be excluded. The most carefully purified "clay" obtained from plastic clays consists of particles which are so small that hitherto their mineral form has not been determined satisfactorily, but they are usually assumed to resemble kaolinite or some amorphous material having an analogous composition and properties.

The mineralogical nature of purified *burned clays* is quite indeterminate. Such crystals as occur in them are either present as impurities in the raw clay or consist chiefly of (*a*) sillimanite (p. 413), formed by the reaction of alumina and silica at a temperature exceeding 1200° C., or (*b*) silicates and aluminates which have crystallised from the glassy matrix formed by the combination and fusion of the various bases with some of the silica in the clay.

Kaolinite is an alumino-silicic acid, the composition of which corresponds to $Al_2O_32SiO_22H_2O$. It may occur as white, grey, or yellowish monoclinic crystals having a hardness of 2·0–2·5, a specific gravity of 2·6, and a refractive index of 1·56.

Hydromica may be a transition form intermediate between kaolinite and sericite. It is often aggregated into rouleaux in a manner similar to kaolinite. It has greater single and double refractions than kaolinite crystals, but less than those of muscovite, mica, and sericite. Hydromica seldom occurs in burned clays, as it is dissociated at about 1150° C., forming an isotropic mass.

Halloysite is a white or slightly tinted substance; it appears to be amorphous and to have the chemical constitution described on p. 345. It has a hardness of about 1·5 and a specific gravity of about 2·1, and when placed in water it swells and falls to powder. It is a very unusual constituent in British clays, though it has been thought that it occurs in Glenboig fireclay and in minute quantities in some of the fireclays and china clays. A crystalline variety having the same composition is termed **pholerite**; another mineral, **lenzenite**, is probably very similar. **Fuller's earth** may also be an impure form of this substance.

Bentonite is an amorphous form of clay found in the Cretaceous beds of Wyoming, U.S.A. It is cream coloured or sometimes brown, and has a very great capacity for absorbing water. It appears to be highly colloidal, though it is almost non-plastic (p. 264). It is very similar in composition to fuller's earth.

Allophane is an amorphous alumino-silicate which occurs as a white, honey-coloured, or wax-yellow substance, though in some cases it is bluish green or brown. Some specimens are translucent, but others are opaque. It has a hardness of 3 and a specific gravity of 1·7–1·8. Its composition is described on p. 345. It rarely occurs in clay.

Collyrite is a dull white amorphous substance, the chemical constitution of which is described on p. 345. It occurs in nodular masses which are somewhat unctuous and plastic. It has a specific gravity of about 2·1.

Nacrite, according to Des Cloizeaux, consists of white, rhombic crystals, having a somewhat pearly appearance and forming a dense aggregate of fine flakes. It has a specific gravity of about 2·67. Nacrite may be distinguished from kaolinite, which has the same chemical composition, by being optically negative, whilst kaolinite is optically positive.

Pyrophyllite occurs as radiating groups of rhombic crystals. For its chemical composition see p. 345.

Montmorillonite occurs as a soft pinkish amorphous material, the chemical composition of which is described on p. 345.

Lithomarge consists of a white or cream-coloured amorphous clayey material similar in composition to kaolin, though some varieties are very aluminous and approach bauxite in character. It is slightly plastic and somewhat unctuous. Analogous minerals are **myelite** (whitish, conchoidal form), **carnalite** (pinkish, compact form), and **tuesite** (bluish).

Other minerals similar to clay, but much contaminated by other substances, also occur. Thus **bole, umber,** and **sienna** consist of ferruginous clayey material of a brownish-yellow or red colour and of very variable composition.

When these various minerals are heated they behave in a manner similar to clay (p. 348), though the other minerals usually present as impurities enter into combination with them and their decomposition products, and so produce so complex a mixture that it is almost impossible to ascertain its mineralogical composition.

Sillimanite ($Al_2O_3SiO_2$) is a comparatively rare mineral, though found in massive form in India. It is of considerable interest, inasmuch as it is formed when clays are heated to a sufficiently high temperature under conditions which permit the sillimanite to crystallise. According to Cross, Iddings, Pierson, and Washington,[1] sillimanite is only formed after all the bases have combined with sufficient silica to produce the most siliceous silicates possible. Sillimanite consists of brown, grey, or greenish orthorhombic crystals which, in calcined clay, usually occur as long, needle-shaped forms or wisp-like aggregates. It has a hardness of 6–7 and a specific gravity of 3·23, and shows strong double refraction. It is unmistakable in thin sections of burned-clay products when the latter are treated with hydrofluoric acid to remove amorphous matter, and are then examined under the microscope.

Sillimanite may be produced artificially by the prolonged heating at a temperature above 1400° C. of a mixture of clay and alumina containing equimolecular proportions of alumina and silica. It is readily observed in hard porcelain and in fireclay pots which have been used for a considerable time in the manufacture of glass of high melting-point.

Sillimanite does not often occur in raw clays, but has been noted in some sands.

Two anhydrous minerals of the same composition are found in nature, namely, **andalusite**, which occurs as grey or reddish orthorhombic crystals with a hardness of 7·58 and a specific gravity of 3·1–3·3, and **cyanite**, which occurs as blue-grey, grey, or blackish triclinic crystals with a hardness of 4–7 and a specific gravity of 3·6–3·7. Both andalusite and cyanite occur to a varying extent in clays, the latter being the more frequent, as it is very stable. When heated, andalusite changes first to cyanite and at a high temperature to sillimanite, the last mentioned being formed, according to Vernadsky, at 1350° C.

Other minerals may also occur in burned clays according to the impurities present in the raw material. These minerals may not be present in a crystalline form, as

[1] *Loc. cit.*, p. 315.

if the temperature has been sufficiently high they may have been fused, producing an isotropic glass which does not readily crystallise on cooling. As some glassy matter is always present in burned clay it is impossible to ascertain completely which minerals are present.

Mineral Impurities in Raw and Burned Clays

The purest clays are those which most nearly resemble a pure alumino-silicic acid, the nearest approach to a pure clay in this country being most carefully prepared specimens of *china clay* from Devon or Cornwall. Commercial china clay of good quality consists almost wholly of a substance—possibly an amorphous or microcrystalline form of kaolinite—which has been variously named "clay substance," "true clay," and "clayite," mixed with a varying proportion of quartz (p. 425), muscovite (mica) (p. 417), tourmaline (p. 418), etc., the best commercial samples apparently containing about 10 per cent. of these impurities. Felspar (p. 416) is seldom found in English china clay, but minute proportions of hydromica (p. 412), epidote (p. 418), zircon (p. 429), titanite (p. 429), rutile (p. 429), and diaspore (p. 339) are frequently found.

The *ball clays* of Dorset and Devon vary greatly in the nature and proportion of impurities present, some of these clays appearing to contain 90 per cent. of alumino-silicic acid, whilst others contain more than 50 per cent. of substances (chiefly free silica) which are not of the nature of clay. Most ball clays contain carbonaceous matter (p. 422), free silica (below), mica (p. 417), and other complex silicates, iron sulphide in the form of pyrites (p. 419), marcasite (p. 419), various iron (p. 418), lime (p. 420), and magnesia (p. 421) compounds. In some cases, soluble alkali salts are also present.

Fireclays and other less pure clays and shales contain similar minerals—present as impurities—to those in ball and china clays, but in larger proportions. The many changes to which the less pure clays have been subjected during oft-repeated transportation and deposition have caused them to become mixed with an indefinite amount of other matter, including sand, felspar, mica, undecomposed rock fragments, and a large number of minerals, many of which are present in quite insignificant proportions, though together they exercise a marked effect on the properties of the clay. In the following pages, only the more important minerals are mentioned, for reasons given on p. 406. Information regarding their chemical effects upon the clays in which they occur will be found by referring to the page mentioned after each mineral.

Silica occurs in clays in the free state either as (*a*) sandy grains of varying sizes, chiefly consisting of quartz, or (*b*) colloidal or amorphous silica. These forms are described on p. 424. The effects of silica on the chemical properties of clay are described on p. 363. In burned clays, the form of the silica grains remains unaltered until a temperature of about Cone 10 is reached, after which the edges of the grains become rounded as a result of partial fusion and of the formation of fusible silicates. If the clay is very impure the silica is then increasingly attacked by the fluxes present, as the heating is prolonged, until at about Cone 18 the silica is wholly dissolved in

the fused glassy matrix composed of a complex mass of molten silicates. If the heating is stopped before this stage is reached, the material will have an intermediate mineralogical composition, the nature of which obviously depends on the duration of the heating and the temperature attained.

In most articles made of fired clay the greater part of the free silica remains as quartz (p. 425), but partial inversion to cristobalite or tridymite (p. 426) frequently occurs, though these allotropic forms of silica are not readily recognised in fired clay products. Hence, in thin sections of red bricks, terra-cotta, etc., the quartz is easily recognised as rounded or sub-angular fragments, which are sometimes clear and transparent, and in other cases are more or less clouded as a result of inclusions of water and other substances. In firebricks which have been burned at a sufficiently high temperature the quartz is less easy to recognise, and in translucent, hard porcelain it is almost wholly dissolved, and forms part of the vitrified mass which gives porcelain its characteristic properties.

Flint may be recognised in microsections of some bricks, etc., as irregular fragments, which may be either transparent, translucent, or opaque, the melted portions being always opaque. At high temperatures, the flint is dissolved, and on cooling the ware it sometimes recrystallises as tridymite or cristobalite, but more frequently it remains as an isotropic glass.

Silicates, Aluminates, and Alumino-silicates.—Any or all of the silicates, aluminates, and alumino-silicates mentioned in Chapter VIII may be present in a clay. In addition, there may be any or all of the following :—

Enstatite, $MgOSiO_2$, is a magnesium silicate (p. 368) which occurs as colourless, grey, green, or brown orthorhombic crystals, with a hardness of 5·5 and a specific gravity of 3·1–3·3. It is so readily decomposed that it is only found to a limited extent in clays.

Hypersthene, $(FeMg)OSiO_2$, is a silicate of magnesium (p. 368) and iron (p. 366) which occurs as brownish-green, green, brown, or black orthorhombic crystals, with a hardness of 5–6 and a specific gravity of 3·5. It is not readily decomposed and, consequently, is fairly common in some clays.

Augite, $Ca(MgFe)(SiO_2)_2$ with $(MgFe)(AlFe)_2SiO_6$, is a silicate or alumino-silicate of calcium (p. 367), magnesium (p. 368), and iron (p. 366), which occurs in greenish-black or black monoclinic crystals, having a hardness of 5–6 and a specific gravity of 3·2–3·5. It is not easily decomposed and, consequently, is often recognised in clays.

The following pyroxenes also occur in some clays : *Bronzite*, $(MgFe)OSiO_2$, a silicate of magnesium (p. 368) and iron (p. 366) ; *Diopside*, $CaMg(SiO_3)_2Ca(MgFe)(SiO_3)_2$, a silicate of magnesium (p. 368) with some iron (p. 366) ; *Diallage*, a mineral similar to diopside and augite ; *Wollastonite*, $CaOSiO_2$, a silicate of calcium (p. 367).

Hornblende is a variable silicate or alumino-silicate of calcium (p. 367), magnesium (p. 368), and iron (p. 366), which sometimes contains silicates and alumino-silicates of sodium (p. 364), and potassium (p. 364) ; it occurs as green or black monoclinic crystals, having a hardness of 5–6 and a specific gravity of 3·0–3·47.

Glaucophane, $NaAlSi_2O_6(FeMg)SiO_3$, is a silicate or alumino-silicate of sodium

(p. 364), iron (p. 366), and magnesium (p. 368), which occurs as bluish particles, with a hardness of 6–6·5 and a specific gravity of 3·0–3·1.

Among the less common amphiboles include *Anthophyllite*, $(MgFe)OSiO_2$, a silicate of magnesium (p. 368) and iron (p. 366); *Tremolite*, $CaO3MgO4SiO_2$, a silicate of calcium (p. 367) and magnesium (p. 368), and *actinolite*, a silicate of calcium (p. 367) and magnesium (p. 368). As amphiboles are readily decomposed and converted into secondary products, they do not occur in large proportions in clays.

The term **olivine,** $2(MgFe)OSiO_2$, includes a group of minerals consisting of silicates of magnesium (p. 368) and iron (p. 366), forming green, brown, or black orthorhombic crystals, having a hardness of 6–7 and a specific gravity of 3–4·2. They are easily decomposed, and are therefore rarely found in clays.

Fayalite is an iron silicate (p. 366) corresponding to the formula $2FeOSiO_2$, occurring as brown or black crystals with a specific gravity of 4–4·2. It does not occur to any great extent in raw ceramic materials, but is common in burned products, most of the iron in silica and fireclay bricks being assumed to be fayalite, though usually it is in the form of a slag-like mass and not as crystals.

Forsterite, $2MgOSiO_2$, is a magnesium silicate (p. 368) which occurs in the form of white or light green crystals. It is not often found in raw materials, except in crystalline limestones and magnesite, but is fairly common in burned refractory materials, especially in impure calcined magnesite.

Serpentine, $3MgO2SiO_22H_2O$, is a hydrous magnesian silicate (p. 368) which occurs as green, yellow, red, brown, or almost black monoclinic crystals, with a hardness of 3–4 and a specific gravity of 2·5–2·6. It sometimes occurs as a decomposition product of olivine.

Glauconite is an amorphous hydrated silicate or alumino-silicate of magnesium (p. 368) and calcium (p. 367) with a varying proportion of iron (p. 366). It has a yellowish to blackish-green or grey-brown colour, a hardness of about 2, and a specific gravity of 2·2–2·4. It occurs chiefly in marine deposits and is a characteristic constituent of the green sand clays and sands, to which it sometimes imparts a greenish or brown colour; on burning, the colour of the glauconite is changed to that of red ferric oxide, which is characteristic of clays burned in an oxidising atmosphere.

Staurolite, $2FeO5Al_2O_34SiO_22H_2O$, is a silicate or alumino-silicate of iron (p. 366), occurring as red, brown, or blackish orthorhombic crystals, with a hardness of 7–7·5 and a specific gravity of 3·7. It is a very stable mineral and frequently occurs in clay deposits.

Nepheline, $K_2O3Na_2O4Al_2O_99SiO_2$, is a sodium-potassium alumino-silicate (p. 364), occurring as white, yellowish-green, or brownish hexagonal crystals, with a hardness of 5·5–6 and a specific gravity of 2·5–2·6. It is of rare occurrence.

Felspar (p. 364) is the name given to a group of alumino-silicates containing one or more of the following metals as bases: potassium, sodium, calcium, and barium. The felspars form isomorphous mixtures and, consequently, may vary very greatly in composition, especially as regards the metals present.

The principal felspars are: *Orthoclase*, $K_2OAl_2O_36SiO_2$, or potassium felspar; *Albite*, $Na_2OAl_2O_36SiO_2$, or sodium felspar; *Anorthite*, $CaOAl_2O_32SiO_2$, or calcium

felspar, and *Celsian*, $BaOAl_2O_32SiO_2$, or barium felspar. Mixtures of sodium and calcium felspars form a sub-class known as plagioclase felspars (some of the members of which have definite names such as bytownite, labradorite, andesine, and oligoclase), whilst *Hyalophane*, $K_2OBaO2Al_2O_3SiO_2$, is intermediate in composition between celsian and orthoclase, and soda-orthoclase is intermediate between orthoclase and albite.

The felspars vary in crystalline structure, orthoclase, hyalophane, and soda-orthoclase being monoclinic, whilst microcline and plagioclase felspars are triclinic. When pure, the felspars are colourless or white, but most specimens are tinged reddish grey, green, or bluish, on account of the presence of impurities. They have a hardness of about 6 and a specific gravity from 2–3. As the properties of different felspars are similar, it is often convenient to regard felspars as a single mineral.

Felspars are frequently found in foreign kaolins, but very seldom in English china clays or fireclays. It is still more unusual to find it in brick and terra-cotta clays.

In burned clay, felspar is very difficult to recognise, as the minute fragments which occur in crude clays are readily fused, though occasionally it may be identified.

Mica (p. 364) is a term used to designate a group of minerals crystallising in the monoclinic system and consisting of alumino-silicates of potassium, sodium, lithium, iron, and magnesium.

The principal micas are :

Muscovite micas, including *muscovite*, $K_2O3Al_2O_36SiO_22H_2O$, or potassium-mica, *paragonite* or sodium-mica, and *lepidolite* or lithium-potassium-mica. Of these, *muscovite* consists of white, black, brown, yellow, or green crystals, with a hardness of 2–2·5 and a specific gravity of 2·85. It usually occurs in thin flat plates or scales. *Paragonite* is similar, but has a hardness of 2·5–3 and a specific gravity of 2·9. *Lepidolite* is of a white grey lilac or rose-red colour, with a hardness of 2·5–4 and a specific gravity of 2·8–2·9.

Muscovite micas are very stable and, consequently, are the form generally found in clays.

Biotite micas, including *biotite*, $(HK)_2(MgFe)_2(AlFe)_2(SiO_4)_3$, or iron magnesium mica ; *zinnwaldite*, or lithium biotite, and *phlogopite*, $AlMg_3KH_2Si_3O_{12}$, or magnesium mica. Of these, *biotite* occurs either as scales or in large massive crystals of a black or dark green colour. In transmitted light the flakes appear brown, green, or blood-red. It has a hardness of 2·5–3 and a specific gravity of 2·7–3·1. On weathering, it alters to chlorite and so is seldom found in clays. *Zinnwaldite* is pale yellow or brown in colour (sp. gr. 2·9–3·1). *Phlogopite* occurs as white, colourless, brown, or copper-red crystals or scales, with a hardness of 2·5–3 and a specific gravity of 2·75.

Any kind of mica, but especially biotite, is objectionable in clays which are required to burn to a good white, as the iron in the mica is liable to produce a buff or brown colour. Mica frequently occurs in unaltered scales and flakes in lightly burned goods, these scales being readily recognised by their bright glistening appearance when examined by reflected light. In transmitted light, dark micas are generally

citron-coloured or light brown, whilst muscovite mica is often quite white and transparent.

Tourmaline is an aluminium borosilicate or a boroalumino-silicate (p. 364), which occurs as black or blue-black hexagonal crystals, with a hardness of 7–7·5 and a specific gravity of 2·98–3·2. It is a very stable mineral and, consequently, is of frequent occurrence in some clays, and is easily recognised in the form of blue needles in crude china clay.

Tourmaline seldom occurs in clays which have been heated to 1150° C., as at this temperature it is usually melted or dissolved in the vitrified mass which occurs in all burned clays.

Chlorite forms a group of hydrous alumino-silicates of iron (p. 366) and magnesium (p. 368), which occur as greenish hexagonal flakes, with a hardness of 1·5 and a specific gravity of 2·5–2·8. As it is readily decomposed, it only occurs in very small proportions in clays.

Epidote, $4CaO3(AlFe)_2O_36SiO_2H_2O$, forms a group of alumino-silicates of iron (p. 366), calcium (p. 367), and sometimes manganese (p. 368), cerium, etc., which occur as green or brownish monoclinic crystals, with a hardness of 6–7 and a specific gravity of 3·25–3·5. *Zoisite*, $4CaO3Al_2O_36SiO_2H_2O$, is a variety of epidote.

Epidote is seldom found in clays which have been heated to a temperature higher than 1150° C., as it appears to melt at or below this temperature.

Cordierite, $4(MgFe)O4Al_2O_310SiO_2H_2O$, is an alumino-silicate of iron (p. 366) and magnesium (p. 368) occurring as bluish orthorhombic crystals, with a hardness of 7–7·5 and a specific gravity of 2·6–2·7.

Iron-bearing Minerals.—The chemical composition of the iron compounds in clay has been described on p. 366. The principal mineral forms are :

Magnetite, Fe_3O_4 (p. 103), which occurs in black cubic crystals, with a hardness of 5·5–6·5 and a specific gravity of 4·9–5·2. Magnetite seldom occurs in raw clays, but is produced by the partial reduction of ferric oxide during the burning of some claywares. It is common in some bricks, and is readily detected by its magnetic properties.

Hæmatite, Fe_2O_3 (p. 97), occurs as steel-grey, iron-black or reddish hexagonal crystals, or as red amorphous particles, with a hardness of 5·5–6·5 and a specific gravity of 4·5–5·3. It does not often occur in clays which have been much exposed to the weather, as it is readily converted into the hydrated form—limonite. In burned clays it is one of the most important colouring agents (p. 109), especially in red bricks, terra-cotta, etc.

It is very probable that little or no free ferric oxide occurs in raw clays, the iron in them being largely in the form of (*a*) an almost colourless hydro-ferro-silicate or ferro-silicic acid, such as nontronite ($Fe_2O_32SiO_22H_2O$), which, on heating, decomposes, liberating free ferric oxide, or (*b*) as limonite.

Limonite, $Fe_2O_3xH_2O$ (p. 97), is a hydrous iron oxide occurring as yellow or brownish amorphous particles, with a hardness of 5–5·5 and a specific gravity of 3·6–4·0. The term limonite is not confined to a single definite chemical compound, but includes an apparently large number of compounds of variable composition, which are probably

colloidal in nature and contain varying proportions of water. The formula by which limonite is usually expressed is $2Fe_2O_3 3H_2O$, but the term is applied to almost any hydrous iron oxide. It is very common in clays and forms one of the principal colouring agents (p. 108) in the raw material. Limonite occurs especially in clays which have been weathered, and many surface clays and weathered outcrops owe their colour to it. It occurs as (*a*) a film over the grains of clay or sand, or (*b*) as irregular nodules scattered through the mass.

On heating, limonite evolves water and forms red ferric oxide. Hence, like the latter, it is a very important source of the red colour to which many clay products owe their characteristic appearance.

Göthite, $Fe_2O_3H_2O$, is a hydrous iron oxide which forms brownish-black yellowish or reddish orthorhombic crystals, or occurs in the massive or fibrous state, with a hardness of 5–5·5 and a specific gravity of 4–4·4. It seldom occurs in clays.

Turgite, $2Fe_2O_3H_2O$, is a similar hydrous iron oxide, which produces a red streak as distinct from the brownish or yellowish streak of göthite. It also contains less water.

Ferrous oxide, FeO, does not occur in raw clays, but it may be produced during the burning of the clay in a reducing atmosphere.

Nontronite, $Fe_2O_3 2SiO_2 2H_2O$, is a form in which iron frequently occurs in clays. It consists of a hydrous iron silicate (p. 366), which occurs as yellow or pale-green monoclinic crystals, usually in the form of thin plates. It is chiefly interesting on account of its composition, which is fully analogous to that of china clay and kaolinite. When heated to redness it dissociates into ferric oxide, silica, and water.

Fayalite, see p. 416.

Pyrites, FeS_2, is a sulphide of iron occurring as yellowish cubic crystals, having a hardness of 6–6·5 and a specific gravity of 4·8–5·1. It is sometimes disseminated in minute grains through the raw clay, or it may form large nodular or fibrous masses, or it may occur in masses resembling small petrified roots ; the last named are sometimes known as *race*. When heated to redness, pyrites evolves half the sulphur in it and later combines with part of the silica in the clay, forming a silicate (fayalite, see p. 416), which readily melts to a dark, fluid slag. This slag, even when finely ground, forms unsightly blotches, the size of which depends on the size and proportion of the grains of pyrites.

Marcasite, FeS_2, is similar in composition to pyrites, but forms orthorhombic crystals. It occurs chiefly in the form of fibrous masses or nodules in the same manner as pyrites. Marcasite is readily oxidised to ferrous sulphate on weathering, and later forms a whitish scum on the dried clay. Pyrites, on the contrary, is not nearly so easily weathered and oxidised.

Pyrrhotine, Fe_nS_{n+1}, is a sulphide of iron forming red, brown, bronze, or copper-coloured hexagonal crystals or occurring in the massive state, with a hardness of 3·5–4·5 and a specific gravity of 4·4–4·65. It is not of frequent occurrence in clays.

Iron sulphides are most common in the Coal Measure fireclays and in the ball clays, though they also occur to a variable extent in other clays. Unlike iron oxides, carbonates, and sulphates, they do not form a pleasant red colour on the ware in the

kilns, but produce small black spots if the grinding has been sufficiently fine ; otherwise, they form relatively large masses of *fused slag*.

Copper-iron sulphides, chiefly in the form of *chalcopyrite*, *bornite*, and *erubescite*, occur in some fireclays, the principal occurrences in this country being in Northumberland, Durham, South Scotland, North Staffordshire, and Shropshire. These copper compounds act in a similar manner to iron pyrites (p. 419), except that they produce greenish-black slag patches instead of black ones.

Ferrous sulphate only occurs in most clay as a soluble salt. It is often produced by the weathering of sulphides of iron ; it has the same general properties as ferrous carbonate.

Chalybite or *siderite*, $FeCO_3$, is an iron carbonate occurring as yellow, brown, or red hexagonal crystals, with a hardness of 3·5–4·5 and a specific gravity of 3·7–3·9. It also occurs in the massive state. It occurs in large proportions in the Clay Ironstone of British coalfields. Chalybite occurs in the Staffordshire marls and in the Coal Measure fireclays. Chalybite may occur in three forms in clays : (*a*) as a film coating the other mineral grains ; (*b*) as minute crystals ; and (*c*) as concretionary masses, sometimes of large dimensions, consisting of chalybite or clay ironstone.

Vivianite, $Fe_3P_2O_8 8H_2O$, is a hydrous phosphate of iron occurring as white, blue, or green monoclinic crystals, with a hardness of 1·5–2 and a specific gravity of 2·66. Vivianite occurs to a very small extent in boulder clays as minute blue crystals, but the proportion is usually negligible.

Many other minerals, including silicates and alumino-silicates, such as *hornblende* (p. 415), *hypersthene* (p. 415), *augite* (p. 415), *olivine* (p. 416), *fayalite* (p. 416), *glaucophane* (p. 415), *glauconite* (p. 416), etc., also contain a variable proportion of iron compounds.

The ferruginous minerals in clays occur as (*a*) large masses scattered irregularly through the mass ; (*b*) minute grains uniformly distributed ; and (*c*) stains on the surface of the grains. The form (*a*) may be removed fairly readily by hand-picking, but the other two forms are almost impossible to remove.

In thin sections of articles made of burned clay, the decomposition products of limonite, hæmatite, and many other iron compounds may be recognised under a microscope (the section being illuminated by reflected light) as brown or reddish-brown specks where the material has been fired in an oxidising atmosphere, and as bluish-black films where a reducing action has occurred. The other minerals present are frequently enveloped by a film of iron oxide.

Pyrites is never seen in microsections of properly burned clayware, as it is decomposed at a comparatively low temperature, forming the vitrified, slag-like material mentioned on p. 419.

Calcium Minerals (p. 367).—The chief calcium compounds in clays are (*a*) *calcite* ($CaCO_3$), which occurs as white or grey hexagonal crystals, with a hardness of 3 and a specific gravity of 2·71, or as amorphous grains ; (*b*) *aragonite* ($CaCO_3$), which occurs as white, grey, or greenish orthorhombic crystals, with a hardness of 3·5–4 and a specific gravity of 2·94, or as amorphous grains ; and (*c*) various calcium silicates and alumino-silicates previously mentioned (pp. 415 to 418). The chief calcium

silicates found in both raw and fired clays are the metasilicate (wollastonite, $CaOSiO_2$) and the orthosilicate ($2CaOSiO_2$). Calcium aluminates do not occur in raw clays, but they do to some extent in burned ones; pentacalcium aluminate ($5CaO3Al_2O_3$), with a melting-point of 1380° C., sometimes occurs; if the clay has been heated above 1530° C. the tricalcium aluminate ($3CaOAl_2O_3$) may be formed; neither of these compounds occur as natural minerals.

Gypsum (calcium sulphate, $CaSO_4$) occurs in some clays and shales in the form of colourless, white, grey, yellow, or reddish monoclinic crystals, with a hardness of 1·5–2 and a specific gravity of 2·3. *Selenite*—another variety of gypsum—is more common in clays, especially the London and Oxford Clays, and in some shales.

Apatite (p. 422), a crystalline calcium phosphate, occasionally occurs in clay, as also may *coprolites* (p. 422) and other calcium phosphates of organic origin. In burned clays various other complex calcium compounds may occur, such as calcium ortho- and metaferrates.

Barium minerals are not of frequent occurrence in clays, the only one of importance being *barytes* (barium sulphate, $BaSO_4$), which occurs as colourless, white, yellow, red, brown, or blue orthorhombic crystals, with a hardness of 2·5–3·5 and a specific gravity of 4·5. Barytes sometimes occur as the cementing medium in clays and shales, as at Seaton in Northumberland. Barium silicates and alumino-silicates are of rare occurrence in some clays.

Strontium minerals seldom occur in appreciable quantities in clay, the only one likely to be recognised being *celestine* (strontium sulphate, $SrSO_4$), which occurs as white orthorhombic crystals, with a hardness of 3–3·5 and a specific gravity of 3·96.

Magnesium minerals (p. 368) occur to a small extent in most clays. They occur chiefly as magnesite (p. 427), dolomite (p. 428), spinel (*below*), cordierite (p. 418), and various magnesium silicates and alumino-silicates. Magnesite sometimes occurs in clays as fibrous crystals, but generally the grains of magnesium compounds are too small to be recognisable as they are difficult to separate mechanically and the proportion is almost invariably less than corrresponds to 3 per cent. of magnesia.

Aluminium minerals (other than clay and the alumino-silicates mentioned previously) sometimes occur in clay. Thus, free alumina may occur as *corundum* (p. 426), bauxite (p. 427), laterite (p. 427), or diaspore (p. 427). Free alumina seldom occurs in clays, though Van Bemmelen has found it in some tropical ones (which are really laterites), consisting probably of a mixture of free silica and free alumina in the colloidal state. Some highly aluminous Scotch fireclays, which are termed "bauxitic fireclays," appear to consist of a mixture of bauxite and clay.

The chief aluminates which occur in clays are known as *spinels*, which term designates a group of minerals consisting essentially of magnesium aluminate, together with some iron, manganese, and chromium aluminates; they occur as red, brown, black, green, or blue cubic crystals, having a hardness of 8 and a specific gravity of 3·5–3·6 (p. 356).

Titanium minerals (p. 428), being very resistant to the action of the weather, are fairly common in some clays, the chief ones being *rutile*, *ilmenite*, *sphene*, *leucoxene*, *anatase*, and *brookite*. The total proportion present seldom exceeds the

equivalent of 3 per cent. of titanium oxide, and in many highly plastic clays less than the equivalent of 1 per cent. of titanium oxide is present. Titanium compounds are very persistent and often remain quite unaltered in clays and other materials which have been fired at 1300° C.

Chromium minerals (p. 429) sometimes occur to a very small extent in clay, usually in the form of *chromite* (p. 429), or occasionally as *spinels* (p. 421).

Tin-bearing minerals seldom occur in clays, though occasionally *cassiterite* (SnO_2) is found as black or brown tetragonal crystals, with a hardness of 6–7 and a specific gravity of 6·4–7·1.

Manganese minerals occasionally occur in clays, chiefly as a thin film of oxide on the other mineral grains.

Phosphate minerals occur in some clays. The most important are *apatite* (p. 421), a phosphate and fluoride of calcium or a phosphate and chloride of calcium, $3Ca_3P_2O_8.CaF_2$ or $3Ca_3P_2O_8.CaCl_2$, which occurs as blue, grey, red, brown, green, or yellowish hexagonal crystals, with a hardness of 5 and a specific gravity of 3·17–3·23.

Coprolites and *phosphorite* are natural phosphates produced by the accumulation of organic remains. Phosphatic nodules of this nature are common in the Greensand beds, and true coprolites are found in the Oxford Clay and Gault formations.

Organic and Carbonaceous matter (p. 430) occurs in clays in very variable proportions according to their mode of formation and the actions to which the clays have been exposed. It is derived chiefly from (*a*) the percolation of water containing humic matter in solution or colloidal suspension or soil in suspension, the matter being absorbed by the pores of the clay and so retained ; (*b*) the deposition of clay upon organic matter or the deposition of organic matter on clay beds, the carbonaceous material being gradually incorporated into the clay ; or (*c*) the admixture of bituminous or carbonaceous rocks with the clay during the deposition of the latter. The carbonaceous matter may be disseminated either in large masses, minute grains, or as films over the surfaces of the other grains. Ball clays usually contain 3–4 per cent., and sometimes as much as 10 per cent., of carbon in the form of an organic jelly derived from peat, lignite, coal, or other organic matter—usually of vegetable origin, or in the form of oleaginous matter derived from fossilised fishes and creatures having shells, which, on heating, produce " shale oil " and gives them a dark colour. Sometimes the plants from which the organic matter has been derived may be identified, but the greater part of it has usually undergone too great a decomposition to be definitely recognisable. All the organic carbon present in a clay may be burned off when the clay is heated to redness in a current of air, but the process requires care, or the mass may be bloated and superficially fused in such a manner as to prevent the oxidisation of all the carbon.

In primary clays, such as china clays and kaolins, organic matter is practically absent ; it is more abundant in plastic clays, such as are used for the manufacture of bricks, tiles, terra-cotta, etc. The chief effects of carbonaceous matter is to impart a dark colour to the raw material (p. 106) ; it also reduces the amount of fuel required for firing the clay.

If the carbonaceous matter is in the form of fine grains uniformly disseminated

through the clay, it is not usually harmful, as it is readily burned out by slowly heating the clay in an oxidising atmosphere, care being taken to avoid surface fusion which seals the pores and prevents all the organic matter from being fully oxidised. Where larger masses of organic matter occur, however, it may cause trouble on account of the amount of heat and gas evolved, causing superficial fusion, and because of the large cavities which are left when the particles of organic matter have been burned away. In all cases where a clay contains sufficient organic matter and sufficient fluxing materials, such as lime or soda compounds, a great difficulty commonly occurs in the firing process, resulting in the production of " black hearts," and sometimes of a highly bloated mass. These objectionable changes are due to the fact that the texture, being very close, prevents the ready access of air to the interior of the articles, with the result that, if much carbonaceous matter is present, before it can be oxidised and removed, the exterior pores of the article become closed with fused material and so effectually prevent the removal of the carbonaceous matter. Unless great care is taken to control the rate of combustion and the rise in the temperature of the mass, superficial fusion may occur, and if this takes place sufficiently it will be impossible to remove the black " core " or to reduce the swelling by any treatment which does not spoil the ware.

Water may be conveniently classed as a mineral. It occurs in three forms :

(*a*) Hygroscopic water (p. 336).
(*b*) Water of formation (p. 269).
(*c*) Combined water (p. 337), including water of crystallisation.

Some other minerals associated with clay also contain combined water, as shown in Table CXXI.

TABLE CXXI.—*Water in Minerals*

	Water, per cent.		Water, Per cent.
Kaolinite . . .	14	Halloysite . . .	20
Muscovite . . .	4–5·5	Nontronite . . .	11
Limonite (average)	14·5	Selenite . . .	21
Allophane . . .	30	Ferrous sulphate . .	46

The effect of water on clays has been described in Chapter VI.

THE MINERALOGICAL COMPOSITION OF SILICA AND SILICEOUS MATERIALS

The principal siliceous materials, other than clays, which are used in the ceramic industries, are (*a*) crystalline silica rocks, including sandstones, ganisters, quartzites, and silica sands ; and (*b*) amorphous or organic silica, including flint, kieselguhr, etc.

Free silica occurs in a variety of forms in nature, and comprises a large portion of the bulk of the earth's crust, something like 60 per cent. of which consists of this mineral, either in bulk or disseminated through other rocks in particles of varying sizes. Free silica occurs in both crystalline and amorphous conditions, the principal forms being the following :—

Amorphous silica occurs as (*a*) precipitated silica formed by the deposition of silica from solution ; (*b*) siliceous skeletons of diatoms, etc., in such forms as kieselguhr, tripoli, etc. ; and (*c*) silica glass, which is of infrequent occurrence in nature, but common in clay products prepared by means of industrial processes.

The chemical constitution of silica has already been described (p. 326).

Precipitated silica occurs in various forms in nature, the commonest being flint, chert, chalcedony, and geyserite. *Flint* consists of silica which has been precipitated around some nucleus of either organic or inorganic matter and, consequently, flints often contain a variable proportion (usually about 5 per cent.) of impurities, chiefly of carbonaceous and calcareous matter. Flint occurs as grey or black nodules of varying size, of great hardness, and breaking with a conchoidal fracture. Roscoe and Schorlemmer consider that it consists of an intimate mixture of amorphous and crystalline silica. Flint is found usually in the form of pebbles, especially on the sea shore, where they often extend over large areas. They also occur in beds of clay—especially those of Cretaceous age—one bed being known as " clay-with-flints." Smaller grains of amorphous silica in the form of sand occur to a varying extent in clays, sands, and similar detrital deposits.

Chert is similar to flint, being formed by the deposition of sponge spicules producing greyish, brown, or black grains of almost crystalline appearance, though in reality it is truly amorphous. The grains occur in beds of clay, sand, and sand-rocks, especially those of Carboniferous age, in which they frequently form large masses of stone.

Chalcedony is a somewhat fibrous form of precipitated silica formed in the same manner as flint and chert. It is regarded by Roscoe and Schorlemmer as consisting of both amorphous and crystalline silica. Hull found that chalcedony gave an X-ray spectrum identical with quartz, though it does not undergo the same changes as quartz when heated. Sosman [1] suggests that it consists partly of crystalline quartz and partly of amorphous threads, the number of interconnected threads being too small to show an inversion point.

Chalcedony varies in colour from white to bluish or brownish and has a hardness of 7 and a specific gravity of 2·55–2·58, a refractive index of about 1·54 (rather less than that of quartz), and a slightly lower birefringence than quartz. *Onyx*, *agate*, and various other minerals resemble chalcedony so closely that for the purpose of the present volume they need not be distinguished therefrom.

Geyserite is a loose, porous form of silica precipitated from solution around hot springs, as in Yellowstone Park, U.S.A., in Iceland, and elsewhere.

Le Chatelierite is the only form of silica glass found in Nature and is of very rare occurrence.

Colloidal silica (p. 252) may occur either (*a*) in bulk as a horny mass in forms such

[1] *Loc. cit.*, p. 327.

as those mentioned above; (*b*) as a cementing material in other rocks, such as quartzites, sandstones, etc.; or (*c*) as an active colloidal substance in clays (p. 327) (see Chapter VI).

Amorphous silica is used to a varying extent for the manufacture of silica bricks and other siliceous materials, such as *kieselguhr bricks*, etc. For the production of refractory articles, amorphous silica has the advantage of being more readily converted into the low specific gravity forms of silica than in quartz. For this reason, bricks, etc., made from amorphous silica are more constant in volume than those made from quartz and similar forms of crystalline silica.

Crystalline silica occurs in nature in three forms, the commonest being quartz, whilst tridymite and cristobalite are relatively rare. Both the latter forms of silica are produced by heating silica to high temperatures, as in the preparation of silica bricks and other siliceous articles.

Quartz occurs as hexagonal or rhombohedral crystals, which are colourless when pure, but are often stained a variety of colours on account of impurities present. Whilst this form is typical of quartz, a closer examination will show the presence, on some crystals, of small triangular facets. The presence of these facets shows that the symmetry of the quartz crystal is restricted to one vertical axis of threefold symmetry. Since no centre of symmetry and no plane of symmetry is present, quartz crystals can exist in two enantiomorphous forms, one of which rotates a ray of polarised light to the left (*i.e.* it is lævo-rotatory) and the other to the right (*i.e.* dextro-rotatory).

The rotatory power of quartz may be represented by the following equation:—

$$a = \frac{K}{L^2 - L_1^2},$$

where a is the angular rotation in degrees per mm., K is a constant=7·1764, L^2 and L_1^2 are the wave-lengths corresponding with the various "free periods" of the electrons of the medium. Where very great exactitude is essential, Lowry prefers to use the equation:

$$a = K + \frac{k_1}{L^2 - L_1^2} + \frac{k_2}{L^2 - L_2^2},$$

where L_1^2=0·012742, L_2^2=0·000974, K=−0·1915, k_1=9·5644, k_2=−2·3114.

For sodium light in which L=0·5889963 μ the rotatory power, a=21·7483° per mm.

Quartz has a conchoidal fracture, a hardness of 7 and a specific gravity of 2·65. Its refractive index is 1·55 and its birefringence 0·009. It is often readily recognised under the microscope by having numerous inclusions which cause it to be cloudy or opaque.

Quartz occurs either in massive form, as small grains disseminated through other rocks or as sand. The most useful forms of massive silica are *quartzites*, which consist of an irregular mosaic of grains of quartz cemented by a siliceous cement, *silica rocks*, which are grains of quartz united by a cement, preferably of a siliceous nature, but generally containing more impurity than quartzites, and *ganisters*, which consist of

grains of quartz with an argillaceous bond. Loose incoherent sands are also of value for making sand-bricks and for the linings of open-hearth and other furnaces. The chemical properties of siliceous materials for making silica, ganister, and similar bricks have been described on p. 398, whilst their physical character is dealt with on p. 18. For information regarding the occurrence and distribution of siliceous sands, see the author's *Sands and Crushed Rocks*. 2 vols. (Frowde, Hodder & Stoughton, Ltd., London).

The impurities in silica rocks are practically the same as those in clay, to which reference has already been made on pp. 414–423.

The impurities in kieselguhr, tripoli, and similar substances are chiefly silt, clay, sand, volcanic ash, and decayed organic matter.

Tridymite occurs as orthorhombic trins or pseudo-hexagonal crystals, with a specific gravity of 2·28 and a refractive index of 1·477. It is not a common constituent of raw ceramic materials, but is often formed in burned siliceous materials and is a very desirable constituent, as bricks and other articles consisting largely of tridymite are constant in volume when heated and are, therefore, less sensitive to sudden changes in temperature than quartz.

Cristobalite occurs as twins belonging to the quadratic system, but giving a pseudo-cubic appearance. It has a specific gravity of 2·32 and a refractive index of 1·484. Like tridymite, it is of rare occurrence in Nature, but is common in silica which has been heated to a high temperature, and is a desirable constituent on account of its constancy of volume.

The identification of various forms of silica under the microscope is dealt with in Chapter XV.

Burned siliceous materials—when pure—contain the same minerals as the raw rocks, except in so far as the quartz is converted into cristobalite or tridymite (*supra*). If the siliceous material is not quite pure, the various minerals constituting the "impurities" will combine with each other and with the free silica to form complex silicates, aluminates, etc. (p. 415), as in clays. The iron compounds found in silica bricks and in similar highly siliceous materials are chiefly in the form of *fayalite* (p. 416), though some *magnetite* (p. 418) is occasionally present.

Mineralogical Composition of Alumina and other Aluminous Materials

Aluminous minerals occur in several forms which may conveniently be divided into three groups: (*a*) clays; (*b*) alumina and aluminium hydrate; and (*c*) other aluminous minerals.

The nature of **clays** has been described on p. 411.

Free alumina occurs in Nature in massive form and as grains disseminated through other materials principally as *corundum* (p. 339), which occurs as grey, green, reddish or yellow hexagonal crystals, having a hardness of 9 and a specific gravity of 3·9–4·1. Artificial corundum is prepared by fusing bauxite, and is being increasingly used as a refractory material on account of its refractoriness, inertness to corrosion, and constancy in volume when heated.

Alumina occurs in a hydrous state as *bauxite* (p. 339), and *laterite* (p. 19), which are amorphous granular materials of a white or brownish colour according to the amount of iron oxide they contain, and also as *diaspore* (p. 339), which consists of white orthorhombic crystals, with a hardness of about 7 and a specific gravity of 3·5 ; and as *gibbsite* ($Al_2O_3 3H_2O$), which usually occurs in concretionary masses and rarely as monoclinic crystals. It has a hardness of 2·5–3·5 and a specific gravity of 2·3–2·4. Bauxite does not appear to be a simple mineral, but an amorphous substance of similar composition to various crystalline aluminous minerals. Lienau has found that some forms correspond to diaspore, others to hydrargillite, whilst still others have a different composition which he terms " true bauxite."

Bauxite is the commonest natural form of alumina, and is used for making aluminous refractory materials, as corundum is too infrequent and laterite is generally too impure. Diaspore has recently been used for this purpose.

Other aluminous minerals are chiefly felspars (p. 416) and other alumino-silicates (p. 415) ; their properties are sufficiently described on the pages mentioned.

The occurrence and distribution of the various aluminium minerals will be found in the author's *Refractory Materials* : *Their Manufacture and Uses*, Second Edition (Griffin, London), and also in *Sands and Crushed Rocks* (Frowde, Hodder & Stoughton, Ltd., London).

The chemical properties of the chief aluminous minerals are described on pp. 402 and 403.

The chief impurities in highly aluminous minerals are clay (p. 411), free silica, usually in the form of quartz (p. 425), and iron compounds (p. 418). Artificially prepared corundum may also contain aluminium carbide.

The Mineralogical Composition of Magnesic Materials

Magnesium compounds may occur either as essential minerals in massive form, in which case they are useful as refractory materials, or disseminated through other ceramic materials as impurities, which increase the amount of vitrified matter or bond, but reduce the refractoriness of the materials in which they occur. The principal magnesium minerals which occur in Nature are as follows :—

Magnesite, $MgCO_3$, occurs as white, grey, yellow, or brown amorphous grains or hexagonal crystals, having a hardness of 3·5–4·5 and a specific gravity of 2·8–3 or more. Several varieties of the massive form occur, differing as regards the proportion of iron carbonate they contain and in their physical texture. Thus, *magnesite spar* (sometimes known as *picolite*, *talcspar*, *bitter spar*, or *gioberite*) is a coarse-grained pure variety of magnesite occurring in white or yellowish masses. *Cryptocrystalline magnesite* is a very fine-grained form, but of similar purity to the coarser variety. *Breunnerite* is an impure form of magnesite containing a large proportion of iron carbonate, which, if excessive, renders the magnesite useless as a refractory material, though a small quantity of iron is an advantage in preparing dead-burned magnesia (p. 401).

The chief impurities in magnesite are serpentine (p. 416), dolomite (p. 428),

quartz (p. 425), iron compounds (p. 418), and various magnesium silicates of too small importance to be described here.

When burned at a sufficiently high temperature, each of these forms of magnesium carbonate loses carbon dioxide and forms magnesia (MgO), which may be amorphous if lightly calcined or crystalline if intensely heated, so that it is *dead-burned* and then cooled slowly. The latter form is desirable in the manufacture of refractory materials (p. 220). *Periclase*—a crystalline form of magnesia—crystallises in the cubic system, occurring usually as octahedra. It has a specific gravity of 3·674 and is thus readily distinguished from the amorphous or α-variety of magnesia, which has a specific gravity of 3·0 or less.

Dolomite, $MgCO_3CaCO_3$, is a mineral composed of calcium and magnesium carbonates in equimolecular proportions. It occurs as white or tinted hexagonal crystals, having a hardness of 3·5–4·0 and a specific gravity of 2·8–2·9. In the massive form it was at one time largely used as a refractory material, but is gradually being replaced by magnesia, which is superior in refractoriness and durability. When burned, it forms a mixture of lime and magnesia.

Magnesian limestone is also composed of calcium and magnesium carbonates, though not necessarily in the proportions required to form dolomite. It is used for the same purposes as dolomite, and also as a source of lime.

The Mineralogical Composition of Calcic (Lime) Materials

The principal natural calcium compounds used in the ceramic industries are calcium carbonate and calcium sulphate. **Calcium carbonate** occurs as limestone—(*a*) in amorphous masses; (*b*) crystallised as calcite (p. 420) or aragonite (p. 420); and (*c*) as shells and allied organic structures. **Calcium sulphate** (gypsum and selenite (p. 421)) occurs in massive form near Newark. Gypsum is chiefly of importance as the source of plaster of Paris, from which are made the "plaster moulds" so extensively used in pottery manufacture. The gypsum ($CaSO_4H_2O$) is heated to a temperature of about 70° C. with constant stirring until it "boils" and evolves half the combined water present, forming plaster ($2CaSO_4H_2O$ or $CaSO_4\frac{1}{2}H_2O$). This material is ground to a "superfine" powder and is then ready for use.

Many other lime compounds—chiefly silicates and alumino-silicates—occur as impurities in clays and other ceramic materials; they are described in the section on impurities in clay (pp. 414–423).

Mineralogical Composition of Titanic Materials

When titanic minerals occur in massive form they may be employed for various purposes, including their use as refractory materials in the form of bricks, blocks, etc. The same minerals also occur as impurities in clays and other ceramic materials, in which form they are undesirable as they act as fluxes at high temperatures and reduce the refractoriness of the material in which they occur.

The chief titanic minerals are as follows :—

Rutile, TiO_2, is a titanium oxide occurring as reddish-brown, yellowish or black tetragonal crystals, with a hardness of 6–6·5 and a specific gravity of 4·2. As it is practically indestructible, it is one of the commonest heavy detrital minerals in clays and is of very wide occurrence. It also occurs in massive form.

Brookite is a titanium oxide of more limited occurrence ; it is found as brown, red, or blackish orthorhombic crystals, with a hardness of 5·5–6 and a specific gravity of 4. It is almost as durable as rutile.

Anatase is a titanium oxide occurring as slender brown, blue, or black tetragonal pyramids, with a hardness of 5·5–6 and a specific gravity of 3·83–3·95. It is of somewhat limited occurrence.

Ilmenite, $FeOTiO_2$, is a very common detrital mineral, consisting of an oxide of iron and titanium ; it occurs as black tetragonal crystals, with a hardness of 5–6 and a specific gravity of 4·5–5·0. In the massive form it is one of the principal sources of titanium oxide for use in refractory materials.

Sphene, $CaOTiO_2SiO_2$, is a calcium titanite and silicate which occurs as brown, green, grey, yellow, or black monoclinic crystals, having a hardness of 5–5·5 and a specific gravity of 3·54. It also occurs in massive form.

Leucoxene is a variety of sphene produced by the alteration of ilmenite and other titanium-bearing minerals.

For further information on titanium minerals see p. 421.

Mineralogical Composition of Zirconium Ores

Zirconia occurs in massive form, pebbles, or small grains, as baddeleyite, and in sands, clays, and similar detrital deposits, as baddeleyite or zircon. The massive form, both of baddeleyite and zircon, are useful as refractory materials, but when disseminated in other ceramic materials they are injurious, because they act as fluxes and reduce the refractoriness of the materials in which they occur.

Baddeleyite (ZrO_2) occurs in São Paulo, Brazil, as black glassy pieces, stony fragments, and pebbles, whilst **zircon** ($ZrSiO_4$) usually occurs as grey, yellow, green, or reddish-brown tetragonal prisms, with a hardness of 7·5 and a specific gravity of 4·7, in detrital deposits, such as sands, clays, etc. It is sometimes concentrated in sand deposits, and then forms a valuable source of refractory sand.

The chief impurities associated with zirconium minerals are heavy detrital materials, principally titanium compounds (*supra*) and iron oxides (p. 418), as well as some of the rare earth minerals, such as monazite, etc. Silica may also occur to a varying extent, chiefly as quartz (p. 425), but also as felspar (p. 416).

The Mineralogical Composition of Chrome Ores

Chromite, $FeOCr_2O_3$, is the material used in the manufacture of chrome bricks ; it occurs sometimes as octahedral crystals, but more often it occurs in massive form, having a granular and compact structure. It is iron-black or brownish black in colour, with a faint submetallic lustre and an uneven fracture. It is brittle, and has

a hardness of 5·5 and a specific gravity of 4·3–4·5. It usually occurs in association with ultrabasic rocks, peridotites, and serpentine rocks. As chromite is very resistant to weathering it may occur in detrital deposits, such as clays, sands, etc., to a varying extent. In New Caledonia some clays are extremely rich in chromite, and are treated in order to recover it.

The chief impurities in chromite are serpentine (p. 416), silica, either free as quartz (p. 425) or combined with various fluxes forming silicates and alumino-silicates.

The Mineralogical Nature of Carbon and Carbon Compounds

Carbonaceous matter may occur (*a*) as a vegetable or animal product (leaves, twigs, branches, roots, etc.) which may be in the natural state or may have undergone very marked structural changes into coal, lignite, peat, humus, etc.; or (*b*) as a mineral (*graphite* or *plumbago*). Both these two groups of carbonaceous material may occur either in massive form or disseminated through other materials as an impurity (see p. 422). In the latter form carbonaceous matter is not generally harmful, as it burns away when the articles are fired in a kiln, and in some cases it may be desirable as a cheap fuel to aid the burning and to increase the porosity and resistance of the ware to sudden changes in temperature. Carbonaceous matter as an impurity is very common in clays, especially ball clays, which sometimes contain 10 per cent. or more (see p. 422). It also occurs in various other ceramic materials, especially in those of Coal Measure age. Thus, the greyness of some sandstones is due to the presence of carbonaceous matter. Kieselguhr contains a varying proportion of carbonaceous matter, in some cases, 30 per cent. or more being present.

When carbon occurs in massive form, it may be as coal or similar substances, or as graphite. Coal and allied materials are extremely valuable as fuel, but (with the exception of sawdust) they are seldom mixed with other raw ceramic materials.

Graphite or plumbago is largely used in the manufacture of carbon bricks, crucibles, etc. It occurs both in the obviously crystalline or apparently amorphous forms, the former being rare. It crystallises in the hexagonal or possibly monoclinic system, but more often occurs as apparently amorphous scales, laminæ, granules, or earthy masses associated with silica, iron oxide, clay, etc. It is an iron-black to steel-grey colour with a metallic lustre, a hardness of 1–2 and a specific gravity of 2–2·3. The chief desirable features in graphite are its chemical composition (p. 404) and its texture (p. 23).

The principal impurity in graphite is free silica (p. 424), with which is usually associated a number of decomposition products.

Carbides and Carboxides have been largely used in recent years in the ceramic industries, especially silicon carbides, whose chemical constitution has been described on p. 357.

Carborundum forms small black crystals, with a hardness rather greater than corundum (9 on Mohs' scale), but less than diamond (10 on Mohs' scale). It has a specific gravity of 3·17–3·21 and a melting-point of 2500° C., though some samples

have been heated to 2700° C. without showing signs of fusion. It begins to decompose into silicon and carbon-dioxide about 2200° C., so that it cannot be used much above this temperature. When pure it should be perfectly white, but owing to the impurities it contains it may be green, grey, or blue-black.

Silundum (p. 357) forms a greenish or greyish crystal, having a hardness of over 9 and a specific gravity of about 3·0.

Firesand (p. 119) is amorphous, but when heated is converted into the crystalline state.

The chief impurities in carbides and carboxides are free silica, as unaltered quartz (p. 425), free carbon as graphite (p. 430), and iron oxides (p. 418).

CHAPTER XI

PHYSICO-CHEMICAL REACTIONS BETWEEN CERAMIC MATERIALS

The reaction of substances with each other forming other substances differing entirely in chemical properties is termed *chemical action*. Some groups of substances combine easily, some with difficulty, and many not at all. When certain combinations occur, heat is given off, whilst others absorb heat. In the first case the temperature rises, in the second it falls. As a rule, elements will combine only in certain proportions (p. 302).

Some of the laws of chemical action and the classification of substances into acids, bases, salts, and neutral substances has been described in Chapter VIII, but many of the chemical reactions which occur in and between ceramic materials are not the result of purely chemical phenomena ; they are controlled and modified by various physical changes to such an extent that a study of chemical reactions will be incomplete, and even misleading, if the various physical changes are not taken into account. Hence, the use of the term *physico-chemical* reactions for such changes.

It has been explained on p. 299 that a chemical reaction involves the destruction of the original substances and the formation of fresh ones, but whilst a physical change involves an alteration in the properties of a substance, it does not involve the formation of a new substance.

Avoidance of Chemical Action.—It is sometimes important to avoid any chemical action occurring between two substances in contact with each other. For example, in constructing the lining of a furnace the materials comprising various sections may be of an acid, basic, or neutral character respectively, and may react in accordance with the principles laid down in Chapter VIII. Such reactions are most undesirable, as the destruction of the lining may imperil the stability of the structure ; if materials capable of reacting with each other remain in contact for a sufficient time, they would be mutually destructive and must, therefore, be separated by an intermediate substance, which is not attacked by either.

When chemical action is to be avoided, care must be taken to prevent the occurrence of conditions favourable to it, such as finely-divided solid or liquid materials, high temperature, and intimate contact. Thus, in the manufacture of materials to be used at high temperatures, such as refractory bricks, retorts, crucibles, saggers, etc., it is very undesirable to mix materials of respectively acid and basic nature, as they will react when heated and will not withstand such high temperatures as either of the materials when used separately.

In order to prevent the reaction of a furnace lining, crucible, or other refractory article with its contents, it is essential to use materials which will not be affected. Hence, an acid-reacting material ought to be heated in a furnace, etc., made of another acid-reacting material, whilst a basic material should be heated in a furnace of basic material. Thus, in the manufacture of steel by a process in which acid slag is produced, the furnace is made of acid (siliceous or fireclay) bricks, whereas, when steel is made by a process in which basic slag is produced, the hearth of the furnace is lined with magnesite, dolomite, or other basic material. Considerations of cost sometimes prevent this rule being followed, as in the case of melting certain glaze frits, in burning limestone, etc., but these special cases do not alter the general correctness of the principle. A knowledge of means of avoiding chemical action is essential in many branches of the ceramic and other industries, it being a general rule that whatever reactions may take place between the contents of a vessel, no such action should take place between the vessel and its contents if this can be avoided.

Chemical Action and Physical Changes.—In many cases when a chemical reaction occurs, chemical change in the composition of the reacting substances is simultaneously accompanied by a physical change in one or more of them. Thus, if an acid is poured upon a carbonate, there is liberated a gas (carbon dioxide) in quite a different state from that in which the carbon and oxygen were previously combined. Similarly, when a piece of coal is burned, it is slowly converted into a mixture of gases instead of remaining in its original (solid) state.

Physical changes in the state of a substance are usually due to the effect of heat, and more rarely to the effect of light, magnetism, electricity, and other physical forces. Chemical changes, on the other hand, appear to be due to a force of a different nature, which is commonly termed " chemical affinity," and is presumed to be due to the electrical charge carried by each electron and the proton in an atom (p. 301).

The extent to which various substances will react with one another also depends largely on their physical state (this, in turn, being related to their temperature); thus, liquids react more readily than solids, and gases more readily than liquids. In each case, this is partly a result of the freedom of the molecules and of their constituent atoms, the ultimate particles in a gas having the maximum mobility, whilst those in some solids have scarcely any freedom of movement.

The ease and rapidity with which compounds react with one another also depends on their stability. A very stable substance in which the valencies or affinities of the various atoms for each other are well balanced will not be easily decomposed, but an unstable, unsaturated compound (p. 305), or one in which the elements are only loosely united, will react readily.

All reactions, when once started, proceed until a state of equilibrium is reached. This state depends on a number of physical factors, such as temperature, pressure, surface tension, electric charge, etc., and if any one of these factors is changed the state of equilibrium will be destroyed and the reaction will proceed further either in its original direction or in the opposite direction. For example, when calcium carbonate (limestone) is heated to 1000° C. in a closed vessel, it is decomposed, forming

lime and carbon-dioxide gas. This decomposition continues until the pressure of the gas reaches a definite critical value. If, as the vessel is closed, the pressure reaches this value, the decomposition will cease, but will start again if a current of air is drawn through the vessel. By continuing to remove the carbon dioxide gas as fast as it is formed, the whole of the calcium carbonate may be decomposed.

If, on the contrary, the lime so produced is subjected to the action of carbon dioxide, the original reaction will be reversed and calcium carbonate will be reformed.

The reaction and its reversal may be shown by two equations :

$$(a)\ CaCO_3 = CaO + CO_2$$
$$(b)\ CaO + CO_2 = CaCO_3$$

For convenience these may be combined, half-arrows being substituted for the sign of equality—

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

The most stable equilibrium which can be produced exists when two substances, each having a great affinity for each other, are combined together. Thus, silicon and oxygen when combined to form silica, produce an exceptionally stable compound, which is highly inert at temperatures below a red heat, though both its constituents (silicon and oxygen) are active elements.

Hence, when acids and bases react with each other, the final equilibrium product will be a substance (salt) in which both the reacting substances are present in maximum proportions. Intermediate states of equilibrium may occur when there is not sufficient of one material to combine with the whole of the other, and under such circumstances a basic salt may be formed if there is a deficiency of acid and an acid salt if there is a deficiency of base. Thus, sodium hydroxide and sulphuric acid may react in two ways :

$$NaHO + H_2SO_4 = NaHSO_4 + H_2O$$
$$2NaHO + H_2SO_4 = Na_2SO_4 + 2H_2O$$

The second equation may also be written in two stages :

$$NaHO + H_2SO_4 = NaHSO_4 + H_2O$$
$$NaHO + NaHSO_4 = Na_2SO_4 + H_2O$$

In the first stage (where there is a deficiency of base), the intermediate "acid salt," $NaHSO_4$, is produced, but is converted into the neutral salt on the addition of more soda.

Similarly, lime and silica can react with each other in various proportions, the product depending on the relative proportion of lime and silica present and on the temperature and other physical conditions. Typical products of the reaction of lime and silica are :

$3CaOSiO_2$ (deficiency of silica).
$CaOSiO_2$ (maximum stability).
$CaO2SiO_2$ (deficiency of base).

Each of these substances can be isolated, but the first and last are only stable so

long as no further supply of the deficient material is added. When the quantity of deficient material is increased, a reaction will occur at a rate depending on the temperature and other physical conditions and a fresh state of equilibrium will be formed.

Chemical reactions always tend to form the most stable compounds possible under the prevailing conditions. Where several substances are present, those which have the greatest affinity for each other will react in proportion to their affinities until a state of equilibrium is reached. In the case of a single acid reacting with a single base, equilibrium (or in this case neutrality) is reached when the maximum amount of neutral substance is formed.

Chemical reactions may occur between matter in the form of either solids, liquids, or gases. Thus, the following reactions are possible :—

1. **Reactions between two solids** are not common at ordinary temperatures, and in most cases, if it occurs at all, it is so slow as to be negligible unless great pressure is applied, as when a mixed explosive is fired by a blow from a hammer. At high temperatures, many solids react upon one another ; thus, lime and silica, when finely powdered and heated to about 800° C., combine to form calcium silicate, the action commencing before either of the substances are in a fluid state. As solid substances are so immobile, at least one of them must usually be in a very fine state of division and in close contact with the other before any combination can occur. The application of pressure, by bringing the particles closer together, facilitates the reaction.

2. **Reactions between a solid and a liquid** are very common and may be exemplified by the corrosive action of acids and alkalies upon various solid substances and by that of fluid slags, etc., upon firebricks and other ceramic materials. The great mobility of the fluid brings the reacting substances into close contact and so facilitates the reaction. It should be noted that the fluid may be composed of one or more substances—either fused or in solution.

3. **Reactions between a solid and a gas** are also common, especially in furnaces, as the gaseous products of combustion exert a chemical action upon the refractory linings as well as upon the contents of the furnace. In an oxidising atmosphere ferrous compounds are oxidised, whilst in a reducing atmosphere ferric compounds are reduced and deprived of some or all of their oxygen. Many changes which take place in metallurgical furnaces are due to reactions between solids and gases.

4. **Reactions between two liquids** are not of much importance in ceramic processes as the latter are chiefly concerned with solid materials.

5. **Reactions between a liquid and a gas** are of minor importance in ceramic processes, though they sometimes occur when molten materials are oxidised or reduced in furnaces or kilns.

6. **Reactions between two gases** often occur, but do not concern the present subject as they do not directly affect any ceramic process.

Types of Chemical Action.—There are five chief kinds of chemical action :

1. *Direct combination*, such as when magnesium and oxygen combine—

$$Mg+O=MgO,$$

or when silica combines with lime—

$$CaO+2SiO_2=CaO2SiO_2.$$

This type of action is very common in ceramic processes, especially during the burning of goods. Other more complex reactions of the same type also take place, *e.g.* the combination of fluxes such as lime, soda, potash, magnesia, etc., with silica and alumina. These are considered in greater detail later.

2. *Displacement by an element or group of elements*, as when magnesium is attacked by hydrochloric acid—

$$Mg+2HCl=MgCl_2+H_2.$$

Reactions involving displacement are not very common in ceramic processes, but are largely used in some metallurgical operations.

3. *Mutual exchange* or *double decomposition*, as when calcium sulphate and sodium carbonate interact—

$$CaSO_4+Na_2CO_3=CaCO_3+Na_2SO_4.$$

In all such reactions, the acid radicle or ion of one base leaves it and becomes combined with another base, the acid radicle or ion previously combined with the latter then combining with the first base. The general equation for all mutual exchanges of this character is—

$$AB+CD=AD+CB.$$

4. A *rearrangement* is said to occur when the atoms in a compound are recombined in a different manner. The classical example of this is the conversion of ammonium cyanite into urea—

$$(CN)O(NH_4)=N_2H_4(CO).$$

A modified form of " rearrangement " probably occurs when alumina and other substances become polymerised on heating or when one form of silica such as quartz is converted into another, such as cristobalite, or *vice versa*. The decomposition of clay into free silica and free alumina and the recombination of the alumina with half the silica to form sillimanite may also be regarded as a rearrangement.

$$H_4Al_2Si_2O_9=2H_2O+Al_2O_3+2SiO_2$$
$$Al_2O_3+SiO_2=Al_2O_3SiO_2.$$

5. *Dissociation* is said to occur when a substance is decomposed into its constituents, as when calcium carbonate is decomposed into lime and carbon dioxide—

$$CaCO_3=CaO+CO_2,$$

or china clay into free silica, alumina, and water—

$$H_4Al_2Si_2O_9=2SiO_2+Al_2O_3+2H_2O.$$

Many instances of dissociation occur in ceramic processes. Thus, clay, bauxite, limestone, magnesite, dolomite, etc., are all dissociated when heated. Many of the impurities in ceramic materials are also dissociated by heat; thus, sulphides and

sulphates are decomposed with the evolution of gas, limonite (ferric hydroxide) loses water and forms ferric oxide, and many hydroxides behave in a similar manner.

Although all chemical reactions can be included in one of the foregoing types, it frequently happens that several reactions succeed one another in such rapid succession that two or more types of reaction may be involved. The types just mentioned should, therefore, be regarded as guides and not as indicating a very marked dividing line between each type.

Some Factors influencing Chemical Reactions

The factors which influence chemical reactions are very numerous and need to be carefully considered if the reactions are to be properly understood. The number of these factors, the difficulty in distinguishing completely the influence of each, and especially the fact that most ceramic reactions occur at high temperatures, is largely responsible for the small amount of definite knowledge concerning the reactions of clays and other ceramic materials. It is, therefore, very desirable to study each known factor more fully, in order to determine its effect on the other factors and on the course of reaction, but the complexity of many ceramic reactions is so great that it is almost impossible, at present, to investigate them completely.

The principal factors which affect the course of chemical reactions between materials used in the ceramic industries are as follows :—

(*a*) Temperature.
(*b*) Time.
(*c*) Pressure.
(*d*) Vapour pressure.
(*e*) Surface tension.
(*f*) Viscosity.
(*g*) Solubility.
(*h*) Selective action.
(*i*) Catalytic action.
(*j*) Nascent action.
(*k*) Conductivity.
(*l*) Electricity.
(*m*) Light.
(*n*) Change of state (fluidity).
(*o*) Intimacy of association.
(*p*) Relative quantity of each substance present.

Heat is by far the most important factor in influencing the rate of chemical reactions between ceramic materials. At low temperatures, most reactions proceed so slowly as almost to be imperceptible, but as the temperature rises—especially if partial fusion occurs—the rate of reaction increases very rapidly. This is largely due to the fact that the mobility of the constituent atoms varies roughly with the temperature.

There is for most substances capable of reacting with each other a " critical " temperature, below which the reaction proceeds so slowly that it may almost be said not to occur, whilst above the critical temperature chemical reaction proceeds rapidly. In some cases, there is an upper limit of temperature which must not be exceeded or the reaction may proceed in an undesirable direction and yield products of no value. Within these two limits is the " working range of temperature," which should usually be ascertained with accuracy if the best results are desired.

The burning of bricks affords a good example of the need for studying the working range of temperature. If the temperature attained in the kiln is too low the bricks will be weak, friable, and unable to resist the weather. If, on the contrary, the temperature has been too high they may have undergone so much fusion as to lose their shape and become useless. Each clay has its own " best temperature," and until this has been ascertained with a fair degree of accuracy, little progress can be made.

It is sometimes stated that " heat decomposes clay," but this is not altogether correct. It would be much better to state that " at a certain temperature clay decomposes," as the latter statement gives a clear idea of what actually occurs. It also shows why a few grains of sand will melt at 1500° C., whilst a brick made of the same material can be exposed for many months to 1700° C., in the wall of a furnace. In the former case the grains, being small, rapidly attain the temperature at which they melt, whereas the brick, being larger and heated under different conditions, never attains the fusion temperature. One end of a refractory brick may be raised to a white heat, whilst the other is cool enough to be held in the fingers ; here again there is ample " heat," but it is not applied in such a manner as to raise the whole of the brick to its fusion temperature.

Similarly, it is less correct to state that " heat converts amorphous magnesia into periclase " than to suggest that, at a certain temperature, the atoms of magnesia are sufficiently free to rearrange themselves in such a manner as to form periclase.

So far as ceramic materials are concerned, a high temperature facilitates reactions merely because, at that temperature, the various atoms are sufficiently mobile to rearrange themselves in a state of maximum equilibrium under the prevailing conditions. If the temperature is lowered, the conditions of equilibrium may no longer exist and a further change or changes may then occur so as to produce a state of equilibrium at the lower temperature. In the case of various bases and silica or of mixtures of various silicates and free silica, the temperature at which reaction occurs varies very greatly. In the case of a mixture of soda, potash, or lime with silica, combination may occur long before any visible change can be observed in the material, but the rate of reaction is very slow compared with that at much higher temperatures.

As most chemical reactions with ceramic materials proceed more rapidly at high temperatures, it is customary to heat the materials to a much higher temperature than that at which the reaction commences. By so doing, the reaction is made to proceed as rapidly as is possible without damage to the material, and much time is saved. Incidentally, other advantages may accrue, as a material fired at a high

temperature is usually much stronger than if only a lower temperature had been reached. In other words, the reaction between the fluxes and silica has proceeded further and a large proportion of " binding material " has been produced.

Le Chatelier's Theorem.—There is always a tendency, if the chemical equilibrium of a mixture is disturbed, for the equilibrium to be restored by the formation of new compounds or by the absorption or evolution of heat. These changes have not been investigated very thoroughly so far as ceramic materials are concerned, but Le Chatelier has summarised what appears to take place as follows :—

If the equilibrium of a system is destroyed by any external means, a reaction will (if the system is sufficiently mobile) take place to an extent sufficient to restore equilibrium, such reaction being opposed to the force which destroyed the original equilibrium. Thus, if the temperature of a system in equilibrium is raised, an endothermal reaction will occur and equilibrium will result. If the temperature of a system in equilibrium is lowered, an exothermal reaction will tend to take place and a new state of equilibrium to be produced.

Time is almost as important as temperature in enabling a chemical reaction to take place. Although the combination of two single atoms may be instantaneous, yet when large numbers of atoms are involved, time must be allowed in order that they may come into contact with each other. Consequently, if the temperature attained is above the minimum required for the reactions to proceed, a sufficiently prolonged heating at that temperature will enable the reaction to progress to completion equally as well as it would do at a much higher temperature, only in the latter case a much shorter time would suffice.

It is a curious fact that no factor in the reactions of ceramic materials is less considered and less wisely used than *time*. In the elementary books on chemistry and physics the experiments suggested are all selected for the speed at which they can be performed, so that most people with an elementary knowledge of chemistry and physics overlook the importance of the effect of time on all reactions and particularly on those of a colloidal nature.

The dispersion or flocculation of a reversible colloid often requires a considerable time and is rarely instantaneous. Hence, tests or experiments of too short a duration are liable to be seriously misleading. This is clearly shown in the case of a fusible clay, or a mixture of clay with some fusible material such as calcium silicate. If the material is only heated for a short time, it will be necessary to raise the temperature very greatly before any signs of fusion can be recognised, whereas if the material be maintained sufficiently long at a much lower temperature, the same amount of fusion will occur.

When relatively large masses of material are concerned, the effect of time is even more marked, because a heating of short duration will not alter the temperature of the interior of the mass and may render worthless observations made upon physico-chemical changes in which sufficient time is not allowed to secure the necessary equilibrium or the ultimate state of the whole system.

This prolonged heating is known in the ceramic industries as " soaking." It is often much more costly than working the kiln at a higher temperature, but the

latter would effect changes in the ware so rapidly that distortion and loss of shape would occur. By allowing the reactions to proceed more slowly (*i.e.* at a lower temperature) these risks are reduced and, in many cases, are wholly avoided. Where the shape of the product is not important, as in melting metal or glass or burning lime, it is usually desirable to work at as high a temperature as can be obtained without damaging the materials, as the reactions then proceed more rapidly and losses due to radiation, etc., are less serious.

A large part of the burner's skill consists in deciding what is the most suitable duration of heating as well as the maximum temperature to be attained. He has to adjust the temperature so as to complete the desired reactions as rapidly as possible, yet without undue risk of causing distortion of the ware by allowing the reactions to proceed too far.

When the temperature of a kiln or furnace is rising slowly it is fairly easy to stop the heating at any desired point. If the temperature is rising rapidly considerable damage may be done after the heating has ceased because of the accumulated heat in the goods and in the structure.

Pressure usually accelerates chemical action, as it brings the reacting particles into closer contact with each other. In some cases (as where a firebrick is heated under a constant pressure until it collapses), the pressure does not greatly affect the reaction, but merely indicates the extent of the changes which have occurred. Experiments made by Spring have indicated that if a piece of dry clay could be subjected to sufficient pressure, the product would be the same as that obtained by raising the clay to a high temperature.

J. H. L. Vogt [1] has shown that pressure has an important influence on the formation of some complex silicates. He states that olivine, monoclinic pyroxene, felspar, spinel, magnetite, etc., may be formed at either high or low pressures; melilite, however, is only formed under a low pressure, and if the pressure is high, olivine or anorthite-bytownite is formed. Leucite occurs in rocks which have been subjected to only a low pressure, whilst microcline, biotite, and garnet occur when the rock during formation has been subjected to high pressure.

Pressure is also important, as it affects the area of contact or intimacy of association of the particles.

Vapour pressure, which is the pressure at which a substance and its vapour are in equilibrium at a definite temperature, often exercises a great influence on the progress of a chemical reaction. The vapour pressure of liquids is much greater than that of solids; it increases rapidly as the temperature rises. When a substance which is decomposed on heating evolves a vapour or gas, which is unable to escape, the decomposition or dissociation continues until the vapour tension of the gaseous product reaches a critical value. The decomposition then ceases no matter how long the heating is continued under the same conditions. If the temperature is raised, decomposition will commence and will continue until the pressure-equilibrium at that temperature is established. Thus, if limestone (calcium carbonate) is heated at 800° C. in an iron tube which has been exhausted of air, the stone will decompose until

[1] *J. Geol.*, **30**, 611–630 (1922).

the vapour tension of the carbon dioxide is equal to 85 mm. of mercury, and will then cease. On heating to 1040° C. further decomposition occurs until a vapour tension equivalent of 520 mm. of mercury is reached.

On cooling, carbon dioxide will be reabsorbed and calcium carbonate reformed as the temperature drops until a vacuum is again established.

The changes in the vapour- or sublimation-pressure is expressed by the following equation :—

$$\frac{dp}{dT} = \frac{pLs}{RT^2},$$

where Ls is the molecular latent heat of decomposition and the vapour formed has the volume $\frac{RT}{p}$ at the temperature T.

The influence of the vapour pressure on the course of a reaction is very important in the lime-burning industry, for unless provision is made in a lime kiln to remove the carbon dioxide as it is formed, the limestone can never, for the reason just mentioned, be completely converted into lime.

The **surface tension** of a fluid affects chemical reactions, especially those which take place between a porous solid and a liquid substance, as the surface tension controls the extent to which the fluid penetrates the pores of the solid mass. For example, the rate at which a refractory brick or other article is corroded by the fused material produced by the action of heat depends partly on the surface tension of the liquid. If the tension is such that the liquid " wets " the solid readily and easily penetrates the pores, the corrosion will be much more rapid than if the fluid and solid were less intimately in contact.

Viscosity has an important effect on chemical action, because changes can only occur when the reacting substances are in intimate contact and a viscous material flows so slowly that it requires a long time to bring the reacting substances into contact. A mobile liquid will react much more vigorously than a viscous liquid with a solid (assuming other factors to be constant).

There are many reactions in ceramic processes which exemplify the effect of viscosity. Thus, slags at their fusing-point are often very viscous and exert little corrosive action upon the bricks with which they come in contact, but if the temperature is raised, many slags become quite mobile and then exert a powerful corrosive action as they flow more readily into the pores of the brick and so expose a greater surface to their action. Most alkaline silicates are very mobile when fused, and consequently, they readily combine with silica or fireclay. Magnesic and ferrous silicates are much more viscous, and as they flow more slowly and penetrate pores less readily, they are much less actively corrosive. Alumino-silicates are usually more viscous than simple silicates and are not generally so corrosive.

As vapours are still more mobile than liquids they may cause a serious amount of corrosion by penetrating into the smallest pores of bricks, etc., where liquids can reach only slowly.

The solubility of one of the reacting substances in the other or in a third substance

usually increases the rate of reaction by bringing them into more intimate contact than would otherwise be the case. As most ceramic materials are insoluble in ordinary liquids, the only case where solubility is concerned is that of the various substances in the fused material produced when the goods are in the kiln or are heated whilst in use. Such molten material—especially if rich in alkaline or calcareous silicates—has a powerful solvent action and will, in time, effect the destruction of almost all ceramic articles. It is to this action that the corrosion of firebricks, crucibles, etc., by slags is due, and the same action is the cause of most of the distortion which occurs when ceramic materials are " overheated."

As the fused material dissolves silica or other substances, it becomes increasingly viscous and eventually becomes saturated. After this has occurred, it loses its corrosive action so long as the temperature is not increased. Upon a rise of temperature, however, the equilibrium is destroyed and solution will continue until a new state of equilibrium corresponding to the higher temperature is established.

The solubility of the product of the reaction also affects the reaction (see *Selective Action*) as an insoluble product is largely removed out of the sphere of action and so prevents a reversal of reaction taking place.

Selective Action.—Where two or more chemical reactions are possible various conditions will determine which one will take place. If some of the substances present have different affinities for the remainder, the reaction will occur between those which have the greatest affinity for each other. If, by the interaction of two substances present with several others, one possible product is volatile, that reaction which yields such a product will generally occur in preference to others which do not involve a change of state. Similarly, if one of the possible products is insoluble in the liquid under the prevailing conditions, the reaction which yields that product will usually take place in preference to any other reaction in which all the products are soluble (see *Phase Rule*, p. 452). The presence of a catalyst (*below*) may also exercise a selective action.

In some cases, chemical action will not occur in the presence of weak acids or bases, but will do so when strong acids or bases are present. This action is termed *disposing affinity*. Thus, the oxides of such a substance may be difficult to form, and when formed may be readily decomposable, whilst the salts of strong acids or the salts produced by the action of strong bases may be quite stable. The precise cause of this mode of action is not known.

Catalytic Action.—The presence of a small proportion of certain substances sometimes causes the interaction of two other materials without which no reaction would occur under the same conditions. A substance which causes such chemical actions to occur without necessarily entering into combination with the products of the reaction is termed a *catalyst*.

It must not be supposed that the catalyst does not enter into combination during the reaction, for, in most cases, the reverse is the case ; what it appears to do is to form an intermediate compound with either or both of the reacting substances, thereby bringing about a combination from which the catalyst is then excluded and so restored to its original free state. The amount of catalyst which is required is

usually extremely small—often a fraction of 1 per cent.—so that it is extremely difficult to investigate its precise action.

Many of the commonest reactions appear not to take place except in the presence of a catalyst. Thus, a mixture of hydrogen and oxygen, if perfectly dry, will not explode, but if even very slightly moist—a tiny drop of water is more than sufficient—they explode readily and form water. The water in this case acts as a catalyst.

Burned clay is a powerful catalyst in some reactions ; thus, if carbon monoxide is passed over red-hot pieces of firebrick the gas is decomposed and carbon is deposited on the firebrick. Hot pieces of firebrick are also used as a catalyst in the Claus-Chance process for the recovery of sulphur from alkali waste.

Catalytic action or *catalysis* plays an important part in some actions occurring in ceramic processes, especially in the conversion of one allotropic form of silica, magnesia, etc., into another, and in the formation of various complex silicates. Thus, Bleininger [1] suggests that the presence of steam and fluorine vapours may convert amorphous into crystalline alumina, though this is denied by Vogt. The action is expressed by Bleininger as :

$$\text{(amorphous) } Al_2O_3+6HF=2AlF_3+3H_2O$$
$$2AlF_3+3H_2O=\text{(crystalline)}Al_2O_3+6HF.$$

According to Pulfrich,[2] biotite, zircon, and tourmaline facilitate the formation of tridymite from other forms of silica. Very small proportions of fluorides appear, as catalysts, to facilitate the formation of sillimanite in calcined clay and increase the volatilisation of silica.

Iron acts as a catalytic agent in the formation of sillimanite. It also combines with free silica produced by the decomposition of the clay and forms ferrosilicon. It has long been known that sodium tungstate greatly facilitates the formation of cristobalite and tridymite in a cooling mass of fused silica and various acids, including phosphoric, boric, molybdic, and tungstic acids have a similar catalytic action, though Quensel has stated that boric acid retards the formation of tridymite.

Lime, ferrous oxide, potash, soda, etc., also act as catalysts, *e.g.* they enable any alumina and iron present in magnesia bricks to combine with magnesia and form spinels. In addition, some of the magnesia is dissolved and recrystallises from the fused material on cooling.

The simplest forms of catalytic action occur apart from ceramic materials, as in the preparation of hydrogen from zinc and an acid. For instance, if pure zinc is placed in pure dilute sulphuric acid no hydrogen will be produced, but if a very small quantity of copper, iron, or any other metal soluble in the acid, or if a metallic salt is added, the evolution of hydrogen commences immediately. The added substance in this case clearly acts as a catalyst. Similarly, with the Twitchel process for the manufacture of fatty acids, in which hydrogen is made to combine with fats and oils at a comparatively low temperature in the presence of a complex sulphuric acid derivative, whereas in the absence of such a catalyst a much higher temperature and a far greater pressure are essential.

[1] *Trans. Amer. Cer. Soc.*, **9**, 455 (1907). [2] *Ton. Zeit.*, **45**, 1127–28 (1921).

In the case of ceramic materials, similar principles appear to apply, but the reactions are more complex.

It should be clearly understood that a catalyst will not cause two substances to combine which would not otherwise do so ; it merely facilitates the combination or the decomposition, as the case may be, by enabling it to take place under more convenient conditions than otherwise. So far as is known, all the reactions which are effected by the aid of a catalyst can take place without its aid, but only under conditions of temperature and pressure which are much more difficult to secure.

The so-called **nascent action** is closely allied to catalysis. It has been found that hydrogen gas from an external source, when bubbled through a solution, may not exert any chemical action on the latter, but if the gas is produced in the liquid itself its chemical action is very pronounced. Thus, hydrogen, passed through a solution of ferric chloride, has no action upon it, but if the hydrogen is generated in a solution of ferric chloride by the action of zinc and hydrochloric acid the ferric chloride is rapidly reduced to ferrous chloride. The active form of hydrogen or of other substances is said to be in the nascent or " new-born " state. Its activity is attributed to the presence of free atoms or ions which would, in the absence of any reacting substance, combine with each other to form molecules and so cease to possess their power of reaction.

The **electrical conductivity** of the substances often affects the rate at which they react upon one another. If they are all non-conductors, any reaction which may occur will take place very slowly. In the presence of an electrolyte the rate of reaction will increase, and if all of the substances are electrolytes, the reaction will usually take place very rapidly. This is in conformity with the ionisation theory, which assumes that all substances are capable, under certain conditions, of splitting up into ions, each of which bears an electric charge (see p. 316).

A current of *electricity* when passed through a mixture will sometimes affect the rate at which they react, but in the case of solid ceramic materials the chief effect of an electric current is to heat and eventually melt the material, as when magnesia or quartz are fused by the passage of an electric current (more usually the current does not pass through the material, the latter being contained in an electrically heated furnace). In the manufacture of carbides, such as carborundum (p. 404), the sole purpose of the electricity is to raise the temperature of the materials until they react.

Many chemical compounds are decomposed when a current of electricity is passed through them, but most ceramic materials are inert in this respect, or the action is inappreciable.

Other *physical* effects of electricity are described in Chapter XIV.

Light is a very important factor in many chemical reactions, such as those which take place in photography and in the oxidation processes occurring in plants and in other ways. The action of light on the chemical action of ceramic materials is not very marked, though sunlight is considered to facilitate the oxidation of impurities during the weathering of clays.

A **change of state** of one or more substances will often affect its power of reaction,

especially if such change is accompanied by the formation of a liquid or gas. Many substances which do not react, or only slightly when in the solid state, will, if one or more is converted into a liquid (either by fusion or solution) or into a gas, react readily. Physico-chemical actions, such as the production of solid solutions, also occur more readily in the presence of a liquid (see *Phase Conditions*, p. 452).

Similarly, two relatively large pieces of material may remain in contact for some time without any appreciable reaction taking place, but if they are ground to a fine powder and then mixed, they may react readily. Thus, lumps of charcoal, sulphur, and nitre are fairly safe, but a powdered mixture of these materials in suitable proportions forms an explosive (gunpowder). The finer the particles of solid material the more rapidly will they react under favourable conditions.

Conversely, if substances which are normally in the liquid or gaseous state are cooled, and so converted into a solid, their power of reaction is usually greatly diminished.

One of the chief reasons for heating solid substances which it is desired should react with one another is that the heating, if sufficiently intense, may cause a change of state of one or more of the substances.

Sometimes a small rise in temperature will greatly increase the intensity of chemical action.

The increase in chemical action which follows a change of state is almost wholly due to the greater ease with which the particles may come into contact with each other (see the next section).

The **intimacy of association** or extent to which the particles are in actual contact with each other is a highly important factor. It is generally agreed that unless the atoms (or ions) of reacting substances come within a very minute distance of each other, so as practically to be in contact, no reaction can occur. In most cases, actual contact appears to be essential, and the greater the area of the surfaces of the materials in contact the greater will be the speed of the reaction. Consequently, the intimacy of association is dependent upon (*a*) the shape of the particles, (*b*) the size of the particles, (*c*) the homogeneity or heterogeneity of the mixture, *i.e.* the extent to which they are mixed together, (*d*) the porosity, in the case of massive materials, and (*e*) the area of surface in actual contact.

If the particles are in the form of thin flat plates, needle-shaped crystals or other shapes with a large surface area and a very small cross-sectional area, reactions will take place more rapidly than with more compact pieces such as spheres, as the former present a greater surface for the same mass of substance and, consequently, they can enter into more intimate contact. For this reason, thin flakes of mica are more harmful as an impurity in clays than the more compact grains of felspar where neither substance is a desirable constituent.

The size of the particles also influences the speed of chemical reaction, because small particles have a larger relative surface area than larger particles. Hence, fine-grained fluxes are more active chemically than coarsely powdered ones, whilst fine-grained refractory materials are more easily corroded than those of a coarser texture. If two solid substances are " badly mixed," any chemical reaction which

may take place between them will clearly be less complete (unless one of the products of the reaction is a liquid) than would be the case if all the particles were very minute and each was in close contact with a particle with which it could react.

If the area of contact between two materials is increased by compressing them (see *Pressure*, p. 440) the possibilities of chemical reaction will be correspondingly increased.

The rate at which chemical action occurs between substances depends also upon the porosity of the mass, as a porous material presents a much larger surface to the action of the reacting substance than if only the exterior surface of the mass were exposed. This is particularly noticeable in the effect of slags or other molten silicates on firebricks, the corrosion being more or less rapid according to the rate at which the flux can penetrate into the pores or interstices of the material. Hence, materials which are highly resistant to corrosion have a dense surface or skin, which prevents or at least hinders the penetration of the slag.

The **relative quantities of the reacting substances** exert an important influence on the extent to which a chemical reaction can take place, and if large quantities are involved, the results may be quite different from that obtained with small quantities. This difference is due to a variety of causes, such as the much greater heat required to permeate the centre of a large mass of low conductivity and the consequent slower rate of reaction of large masses.

If a material is in large compact pieces of approximately cubic or spherical shape the rate at which they can react and the extent to which the reaction can proceed must be very small unless the conditions are such that the products of the reaction are removed as soon as they are formed. Thus, iron filings can only be completely oxidised by steam when a very large surface of iron is exposed, and conversely, iron oxide can only be reduced completely to metallic iron when a very large volume of hydrogen—much in excess of that actually needed to combine with the oxygen—is present. The mass of the available materials appears to affect the reaction quite apart from the penetrability of the solid material concerned. Thus, a typical example of mass action is shown by the fact that, whilst many silicates are unaffected by powerful acids in the laboratory, they are readily decomposed by feeble acids (such as a solution of carbon dioxide in water) when exposed in large quantities, as in the "weathering" of natural rocks (p. 506).

What is sometimes termed the *law of mass action* states that, broadly, a reaction will proceed further or more easily if the masses of the reacting substances are large than if they are small, but the results in any given case are subject to various other factors, such as those mentioned in the preceding pages.

Not only the total mass, but the relative proportion of the product exerts an important influence on the progress of the reaction. Thus, the reaction represented by the equation

$$CO+H_2O=CO_2+H_2$$

does not proceed to completion if it takes place at or above 1000° C.; in fact, more than half the water remains unaltered after the reaction has ceased. Conversely, if

the reaction takes place in the opposite direction the same relative proportions of the same substances will be found in the product, only a little more than half of the carbon dioxide and hydrogen having united. By varying the temperature and pressure, the reaction may be made to proceed further in one direction or the other, more steam being reduced or more hydrogen oxidised, but the reaction is never completed if the reacting substances are present in the relative quantities apparently required by the equation. The final product will depend on which substance in it preponderates, as this preponderant substance determines the state of equilibrium. Hence, as a result of the relative effect of the masses involved, chemical reactions may be reversed by altering the respective masses of the reacting substances.

In accordance with the law of mass action, when a state of equilibrium is attained, the product of the partial pressures of the substances formed in a reaction, each raised to a power which is the coefficient of its formula in the chemical equation, divided by the product of the partial pressures of the reacting substances, each raised to a power which is the coefficient of its formula in the chemical equation, is constant. Thus, in the reaction

$$A + B = C + D,$$

the quantity

$$\frac{pC \times pD}{pA \times pB}$$

is constant at any temperature.

In an equilibrium expression the partial pressures of the products of a reaction are generally written in the numerator. Thus, the equilibrium expression of the equation

$$CO + H_2O = CO_2 + H_2$$

is usually represented by

$$\frac{pCO_2 pH_2}{pCO pH_2O}.$$

From the foregoing, it follows that, at any given temperature, chemical equilibrium is established when the partial pressures of the reacting constituents equals the product of the partial pressures of the resultant substances multiplied by a constant depending on the nature of the reacting materials.

The same mode of expression can be applied to two-phase systems, except that the partial pressure of solids, being very small, may be omitted. Thus, the equilibrium expression of the dissociation of calcium carbonate to lime and carbon dioxide

$$\underset{\text{(solid)}}{CaCO_3} = \underset{\text{(solid)}}{CaO} + \underset{\text{(gas)}}{CO_2}$$

is as follows :—

$$\frac{pCaO\,pCO_2}{pCaCO_3} = K,$$

or, omitting the partial pressures of the solids,

$$pCO_2 = K.$$

A further result of the laws of mass action is that the velocity of a chemical reaction is directly proportional to the concentration of each reacting constituent.

In the equation

$$CaCl_2 + H_2SO_4 \rightleftharpoons CaSO_4 + 2HCl.$$

If a molecules of $CaCl_2$ are heated with b molecules of H_2SO_4, x molecules of $CaSO_4$ and $2x$ molecules of HCl will be formed and the equilibrium constant (K) will be equal to

$$\frac{x(2x)^2}{(a-x)(b-x)},$$

so that if the same quantity of *any* soluble chloride whose sulphate is also soluble is treated with sulphuric acid, under similar conditions of concentration and temperature the same number of molecules (x) of sulphate must be produced, but if the solubility of the sulphate is such that x molecules cannot remain in solution, a precipitation of the sulphate must occur.

All solids—even the most " insoluble "—have a specific solubility in every liquid ; hence, in solid-liquid systems, the equilibrium is fairly simple, but where a gas is formed a different condition arises. Thus, in the system just mentioned :

$$CaCO_3 \rightleftharpoons CaO + CO_2,$$

if the vapour pressures are a, b, and c, then, since the concentrations are proportional to the pressure,

$$K = \frac{bc}{a},$$

but a and b are constant because they relate to solid $CaCO_3$ and CaO, hence the equation becomes

$$K = c.$$

Hence, the pressure of CO_2 has a fixed value at every temperature. This is known as the dissociation value of $CaCO_3$.

According to Guldberg and Waage, " In a system of reacting bodies, the effect of each substance is proportional to its concentration, and the total effect is proportional to the product of the molecular concentration of the reacting substances."

Mass action plays a very important part in some processes connected with the ceramic industries ; in the formation of some of the raw materials, it enables weak acids to do what cannot, on a small scale, be accomplished by much stronger acids (see p. 506). It largely determines the progress of reactions involving the decomposition of rock-masses by water, such hydrolysis occurring in accordance with the law of mass action and its extent depending on the equilibrium expression and the concentration of the ions of the reacting substances.

In the case of the substances produced by methods of manufacture or during the use of ceramic materials, the final products are largely dependent on the effect of mass action, as the temperatures to which ceramic materials are heated are seldom sufficient

to produce complete fusion, in which state the reactions between the various substances take place with the greatest rapidity. Consequently, the reactions are seldom complete and their progress depends upon the temperature and duration of the heating, as well as on the quantities of the various materials employed. In a thin tile or vase exposed on all sides to the heat of the kiln, the amount of fused material and of the various reaction products will be much greater in proportion to the size of the article than they would be in a solid cubic mass of the same material having the same total volume, because the heat will penetrate the former article much more readily than the latter. In this case, the mass has the effect of delaying the progress of the reaction.

The Speed of Reaction

Chemical reactions do not occur instantaneously, but at a measurable rate, which may vary from that of an explosion to one as slow as the hydrolysis of some rocks.

The speed of a chemical reaction is, other things being constant, proportional to the chemical affinity of the chief substances taking part in the reaction. Wilhelmy's law states that "the velocity of any chemical action at any instant is proportional to the concentration of the reacting substances." The velocity of a reaction may be very low at first, but after an interval the theoretical velocity is attained.

The velocity of a chemical reaction depends on the number of collisions between the reacting molecules per unit of time. This number is influenced by

(*a*) the temperature,
(*b*) the concentration

of the system. Thus, if V = the velocity and a and b are concentrations of the reacting substances $V\rightarrow = K_1ab$, and that of the back reaction is $\leftarrow V = K_2cd$. When $V\rightarrow = \leftarrow V$

$$\frac{ab}{cd} = \frac{K_2}{K_1} = K.$$

K is the equilibrium constant of the reaction $A + B \rightleftharpoons C + D$, whilst K_1 and K_2 are known as the affinity- or velocity-constants of the reaction.

According to the law of mass action, if one product of the reaction escapes as a gas the concentration of the other product must increase and those of the original solutions must decrease. Hence, if

$$K_0 = \frac{cd}{ab}$$

and the concentration of d is lowered, that of c must decrease so that the equation will proceed to the right. If the reaction is more complex, as when

$$2A + 3B \rightleftharpoons 2C + D$$
$$V\rightarrow = K_1a \times a \times b \times b \times b$$
$$= K_1a^2b^3$$

Hence,

$$K = \frac{a^p b^q}{c^r d^s}$$

is the most general expression of the Law of Mass Action.

The velocity of a chemical reaction may also be expressed as a ratio of chemical affinity : resistance to chemical action, *i.e.*

$$\text{Velocity} = \frac{\text{chemical affinity}}{\text{resistance.}}$$

The resistance will depend upon the extent to which the conditions are favourable. These have been described in the preceding pages (pp. 437–449).

The speed at which a given reaction will take place can seldom be predicted in the case of ceramic materials, as the conditions are usually too complex. The speed must, therefore, be found by actual measurement. The velocity of reaction is usually expressed as the ratio between the amount of transformed substances and the time required for the transformation, the amounts of substances being calculated in molecular units, the results being stated in " molecules per minute."

The velocity of reaction between two ceramic substances is sometimes of considerable importance—(*a*) when it is desired to effect a reaction in the quickest possible manner, as in preparing various chemical compounds, glazes, frits, etc., and (*b*) when it is desired to delay the completion of a reaction because such completion would involve loss of shape or other undesirable consequences.

The velocity of reaction is usually increased by raising the temperature at which the reaction occurs and is diminished by cooling. It is also increased by using finely ground materials in the case of solids and by any mechanical means, such as stirring, which will bring the particles into more intimate contact with one another. If means can be employed for removing the products of the reaction as soon as they are formed the reaction will proceed to completion more rapidly than if no such removal occurs. Hence, if it is desired to produce a glass or definite silicate, the velocity of reaction will be greatest if the materials are fused and stirred together, but if it is essential that the pieces of material shall retain their shape (as in the manufacture of porcelain ware) the temperature must not be allowed to rise too rapidly, but must be maintained constant under such conditions that the desired reactions will occur more slowly and under better control.

Reversible and Irreversible Reactions

The terms reversible and irreversible reactions are used to denote chemical reactions which will or will not proceed in opposite directions when the relative masses of the reacting constituents are changed. In an **irreversible** reaction, the products cannot, by any simple change in the conditions, such as by varying the temperature or adding an excess of one of the products, be reconverted into the original materials which existed prior to the reaction taking place. Thus, when nontronite is heated

it is decomposed with evolution of water

$$Fe_2O_32SiO_22H_2O = Fe_2O_3 + 2SiO_2 + 2H_2O,$$

but under no circumstances yet discovered can a mixture of ferric oxide, silica, and water form nontronite. The decomposition of clay is another example of irreversible reactions.

In a **reversible** reaction, on the contrary, the original substances may be reformed by a simple change in the conditions or in the proportions of the product. Thus, when a chemical action occurs and the products of the reaction are not removed, a certain point of equilibrium may be reached at which the action may proceed indifferently in either direction, though no equilibrium-point may be apparent at ordinary temperatures. For instance, at 100° C., the reaction between barium carbonate and sodium sulphate is reversible :

$$BaSO_4 + Na_2CO_3 \rightleftharpoons BaCO_3 + Na_2SO_4.$$

The system is in equilibrium when there are 5 parts of sodium carbonate to 1 part of barium sulphate. With greater concentrations of barium sulphate the latter is decomposed, and with smaller concentrations barium carbonate is decomposed. Thus, in a solution of these salts, either heavy spar or witherite may be deposited, according to the relative proportions of each and the temperature of the solution.

The action of heat upon calcium carbonate also involves a reversible reaction :

$$CaCO_3 \rightleftharpoons CaO+CO_2.$$

The dissociation of the calcium carbonate occurs only when its dissociation tension exceeds the vapour pressure of the carbon dioxide present in the system. As soon as the latter becomes greater than the former, lime and carbon dioxide recombine to form calcium carbonate (p. 434).

Among the numerous reversible reactions which occur in Nature, the following are of special interest in connection with ceramic materials :—

$$\underset{\text{Albite.}}{Na_2OAl_2O_3(SiO_2)_6}+2H_2O \rightleftharpoons \underset{\text{Analcime.}}{Na_2OAl_2O_3(SiO_2)_4}2H_2O+2SiO_2$$

$$\underset{\text{Serpentine.}}{2H_2O3MgO(SiO_2)_3} \rightleftharpoons \underset{\text{Enstatite.}}{MgSiO_3}+\underset{\text{Olivine.}}{Mg_2SiO_4}+2H_2O$$

$$\underset{\text{Anorthite.}}{CaOAl_2O_3(SiO_2)_2}+\underset{\text{Olivine.}}{Mg_2SiO_4} \rightleftharpoons \underset{\text{Augite.}}{(MgOAl_2O_3)(CaOMgO(SiO_2)_3)}.$$

The proportions of these substances which exist in any mineral depend on the conditions necessary to produce equilibrium at the temperature and pressure of the system.

Whenever a reversible reaction can occur and the products of the reaction cannot escape, the condition of equilibrium persists and such a reaction may, therefore, be termed a *balanced reaction.*

The distribution of the reacting masses, when in equilibrium, is determined by the relative concentration of the changing substances, as previously explained.

Until comparatively recent times the existence of equilibrium reactions was unknown; at present the tendency is to regard all reactions as equilibrium reactions, and that even where they appear to be complete, to consider them as only in apparent completion, *i.e.* in reality, the equilibrium merely lies so far to one side as not easily to be disturbed. If this view is adopted, it will be seen that balanced or equilibrium reactions are especially common in the case of ceramic and other materials which may exist in two or more allotropic forms such as silica, magnesia, etc., the particular form present being then largely dependent on the temperature and pressure. Balanced reactions are equally important in the case of many ceramic products, especially those in which a considerable amount of vitrification has occurred, as in porcelain, stoneware, etc., and in glazes, because the composition of such material depends very largely on the nature of the mixture and its state of equilibrium. This subject is dealt with more fully in the sections on *Phase Conditions* (below) and *Equilibrium Diagrams* (p. 454).

Phase Conditions in Chemical Systems

The reactions familiar to students of elementary chemistry are, for the most part, of a simple nature, and some of those which are, in reality, complex are treated as though they were simple. When studying ceramic materials, on the contrary, considerable complexity is unavoidable on account of the impurities present in the materials increasing indefinitely the number of reacting substances and of the factors which influence the results. Thus, whilst the reaction between two pure substances may be as simple as shown by the types of chemical action on p. 435, when one or more slightly impure substances are heated—especially if much fused material in the fluid state is produced—many complex phenomena may arise, these being due partly to physical and partly to chemical phenomena. They may all be included under the term "phase conditions," and in this connection may be studied in greater detail and with greater facility than if each reaction is taken separately.

Matter may exist in three forms or states (namely, as a solid, liquid, or gas), which are conveniently termed *phases*; thus, a substance may exist as a solid phase, liquid phase, or gaseous phase. For example, the compound expressed by the formula H_2O is known to exist as ice (solid phase), water (liquid phase), and steam (gaseous phase). The particular phase in which any substance exists at any given moment depends upon the conditions then prevailing, and when a substance is in the phase conformable to any particular set of conditions it is said to be in equilibrium. Thus, if a drop of water is allowed to fall on a red-hot plate at a temperature of about 900° C. the greater part of the water may remain in the liquid state for a short time, because the steam produced from that part of the drop which is in immediate contact with the hot plate may act as a "buffer." The rapid movement of the drop and the comparatively short time it retains its liquid form show clearly that the liquid state is not the one in which an equilibrium can be maintained. On the contrary, the water is rapidly converted into steam, as that is the gaseous phase which is stable at temperatures above 100° C.

Students of ceramic materials have received invaluable assistance from a formula devised by Willard Gibbs and known as *the phase rule.*[1] In accordance with this rule, the conditions under which any given series of phases can exist is expressed by the equation

$$P+V=C+2,$$

where P is the number of phases in the system, V is the number of external conditions which may be stipulated, and C is the minimum number of components. The *number of phases* may be defined as the number of different homogeneous parts which may exist under the prevailing conditions.

The *number of external conditions* (represented by the symbol V) is usually either 1 or 2, the fixed conditions being generally temperature and pressure, though other conditions may be fixed, if required. In most cases they play a minor part and so need only be considered when the subject is being investigated exhaustively.

A *component* may be either an element or a compound, as its composition does not enter into the definition of a component. Each different substance which may be present, as a separate entity, in the system is a component.

A *system* is the whole, composed of all the components in a state of equilibrium.

A eutectic is not a phase, because it contains two phases. In a homogeneous system there can only be one phase; in a heterogeneous system there may be two or more phases.

The *degree of freedom* or variation of a system is the number of independent variables which must be fixed before the state of the system can be clearly defined.

In the condition of equilibrium of three two-phase systems—solid-vapour, vapour-liquid, and solid-liquid—which meet at a point (the so-called *triple* point) the system is invariant.

As a simple illustration, water may be considered. This substance can exist in three phases, namely, ice, water, and steam. These three phases together form a system in which there is one component, namely, the compound dihydrogen oxide (H_2O). Substituting in Gibbs' rule the respective values for P and C the equation becomes

$$3+V=1+2.$$

Hence, $V=0$, so that under no conditions can all three phases exist simultaneously in equilibrium. If it is assumed that $P=2$ then $V=1$, or conversely, when one condition (*e.g.* either temperature or pressure) is specified as fixed, two phases may exist in equilibrium. If $V=2$, as when a definite temperature and a definite pressure are specified, $P=1$, so that only one phase could exist under the specific conditions.

In the ice-water-steam system there is only one component, but Gibbs' rule is equally applicable where there are several components. Thus, the conditions of equilibrium of calcium carbonate involve three phases, namely, solid (calcium carbonate), solid (lime), and gaseous (carbon dioxide), so that calcium carbonate forms a three-phase system. Calcium carbonate may be resolved into two com-

[1] For a detailed explanation of this rule and some of its applications to other branches of chemistry, see *The Phase Rule*, by Findlay (Longmans, Green & Co.).

ponents—calcium oxide and carbon dioxide—so that C=2, and on substituting this in Gibbs' rule, the equation becomes

$$P+V=2+2,$$

i.e.

$$P+V=4.$$

If only one condition is fixed, *i.e.* V=1, then P=3, the three phases can exist only at one definite temperature or pressure. For example, at 600° C. and at all pressures, all three phases can exist simultaneously, but if both the temperature and the pressure are fixed, V=2 and P=2, so that only two phases could exist under those conditions.

Granite, composed of quartz, felspar, and mica, has three components (alumina, silica, potash) and three solid phases (mica, quartz, and felspar). It is, therefore, univariant. It is also in equilibrium because, not being at a transition-point, it can survive small variations in temperature without changing the state of the system.

The phase rule is very valuable because

1. It permits the classification of systems of similar behaviour.
2. It shows whether the phases of a heterogeneous system are those necessary for equilibrium.
3. It assists in identifying chemical individuals among a series of basic salts or solid solutions.

Gibbs' rule is capable of very wide application and is not limited by the complexity of the factors represented by the symbols P, C, and V. It is, however, qualitative rather than quantitative in its nature, because it does not show which phases will occur, where only a limited number are possible, and it only states the maximum number of phases which could possibly occur. Its value is, therefore, limited to showing the maximum value for each of the symbols P, C, and V in any system. When the particular nature of the factors represented by the symbols is required to be known, another method must be adopted, namely, an equilibrium diagram or phase diagram.

The chief value of the phase rule consists in its power of indicating the maximum value of one or more of the symbols in a given system. In some cases, where this value is unity no further investigation is necessary, but if, for instance, the rule is employed to determine how many phases can occur in a given system and that number is greater than unity, the use of a phase diagram may be essential if it is desired to ascertain the nature of the possible phases.

The chief difficulty experienced in using the phase rule lies in ascertaining what are the precise components, as in complex cases their nature is very difficult to determine.

Equilibrium or Phase Diagrams

An equilibrium or phase diagram is one which shows what phases can exist under given conditions, the latter being usually one of the following pairs :—

(*a*) Temperature and pressure,
(*b*) Temperature and composition, and
(*c*) Temperature and time (p. 464),
but any other conditions may be considered if desired.

It is usually best to limit the conditions to two or at most three, as otherwise the diagrams become so complex as to be almost illegible. When only two variables are considered a plane diagram suffices, one variable being represented by the *ordinates* or horizontal lines proceeding from a vertical scale at the side of the diagram, and the other by the *abscissæ* or vertical lines rising from a scale at the base of the diagram. If, for example, there is only one component (*i.e.* C=1), and the temperature and pressure are regarded as fixed (*i.e.* V=2), then, according to Gibbs' phase rule,

$$P+V=C+2$$
$$P+2=1+2$$
$$P=1,$$

so that only one phase can exist for any given temperature and pressure, though a different phase may exist at different temperatures and pressures. Hence, the phase diagram will show which phase is stable under any particular conditions of temperature and pressure. This is clearly shown by fig. 22, which is the equilibrium diagram of water and indicates the state of water at any given temperature and pressure.

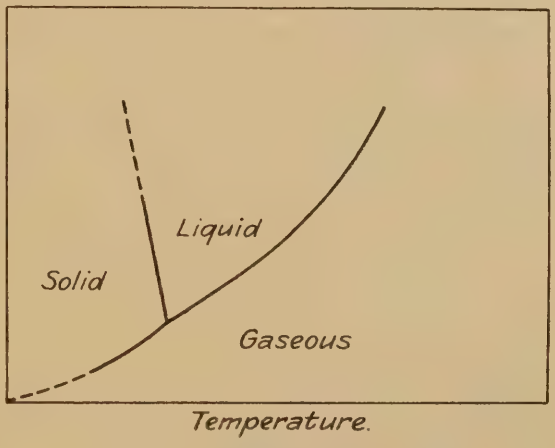


Fig. 22.—Phase Diagram of Water.

When there are three phases and two components in a system

$$3+V=2+2 \text{ or } V=1,$$

the phase diagram can only show one stipulated condition. When this is the temperature it may be plotted as ordinates, whilst the composition is plotted as abscissæ.

The temperature-composition diagrams of reactions in ceramic processes are generally concerned only with the solid and liquid phases, as such materials are seldom volatilised. They may also be termed " melting- or fusing-point diagrams," as they show the dividing line between the solid and liquid phases of the constituents present.

Temperature-composition diagrams are often much more complicated than those showing temperature and pressure in systems having a single component, because various kinds of chemical action, solution, precipitation, etc., may occur between the components under the particular conditions of temperature indicated. Conse-

quently, various different types of graphs may be obtained. These may be divided into three classes according to the changes which occur, as follows :—

(*a*) The substances may dissolve in each other in all or some proportions forming a solid solution.

(*b*) The substances may form an eutectic.

(*c*) The substances may combine to form a chemical compound.

A **solid solution** is a substance which appears to be solid and has many of the characteristics of a solid and yet behaves, in some respects, as a solution. The conception of a solid substance dissolved in a liquid is familiar ; that of one solid substance dissolved in another is less familiar but is wholly analogous. Just as a liquid solution appears to be homogeneous so that it is impossible by inspection to distinguish between the solvent and the solute or dissolved substance, it is equally impossible in the case of a solid solution, as the latter is equally homogeneous like *glass*, which is a typical solid solution. The analogy may be carried still further by comparing the behaviour of an ordinary hot saturated solution with that of a molten mass which if left to itself would form a solid solution. Both these liquids, if cooled under favourable conditions, will produce crystals. In the former, it is agreed that the compound of which the crystals are composed existed in the solution. In the latter, it is not so generally accepted that the crystallising compound is actually present in solution, though by analogy it should be so.

Solid solutions may be (*a*) vitreous, or (*b*) crystalline, depending on the nature of the components and the manner in which the solution has been formed. The general term solid solution is applied both to amorphous and crystalline substances, but especially to amorphous ones ; the crystalline forms are often termed *mixed crystals*.

Just as some liquids can be mixed in all proportions, so some substances form solid solutions in all proportions, whilst others only form such solutions in definite proportions and in addition may form an eutectic (p. 459) or definite chemical compounds (p. 462).

Although there are no general rules regulating the solubility of liquids in each other, it is generally true that those of the same chemical type are so uble in each other, whilst liquids of different types have only a slight attraction for each other. This applies both to ordinary liquids and to fused solids and explains why minerals of the same chemical type are often soluble in each other in all proportions. Thus, some silicates form solid solutions or mixed crystals in whatever proportions they are mixed.

When a temperature-composition diagram of two substances which are wholly miscible in each other is drawn, either of two types of graph may be obtained, namely, (*a*) a plain continuous curve, or (*b*) a curve with a transition-point, showing that an abrupt change in composition occurs at the critical temperature.

Solid solutions differ from definite chemical compounds inasmuch as the latter have a definite melting-point, whereas the former have a range of fusion. This distinction must not be pressed unduly, especially with refractory materials. The simplest type of plain curve (without a transition-point) is shown in fig. 23 ; in

this, the graph consists of a straight line joining the melting-points of the two substances forming the components of the mixture. Such a graph is typical of

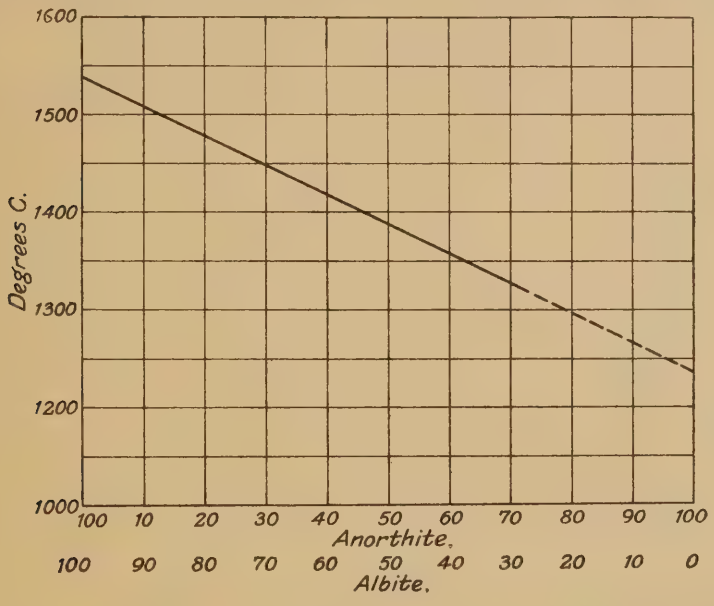


FIG. 23.—ALBITE-ANORTHITE PHASE DIAGRAM.

mixtures of albite and anorthite felspars (p. 416) and of other ceramic materials which do not react on each other.

On examining such a graph, it will be seen that any increase in the proportion of the substance melting at A° will increase the melting-point of the mixture, whilst an increase of the material melting at B° will decrease the melting-point of the mixture. More often, however, a definite curve is obtained when the fusing-points of various mixtures are plotted; the form of the graph is that of a continuous curve, such as that shown in fig. 24, in which the line ACHB is the temperature curve of apparent solidification.

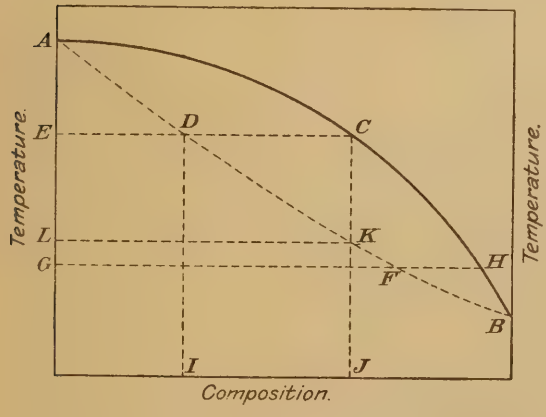


FIG. 24.—PHASE DIAGRAM OF WHOLLY MISCIBLE LIQUIDS.

When a molten mixture of any composition or a solution of several substances commences to freeze it deposits, at first, a solid substance which is poorer in one substance than the mixture as a whole. As the temperature falls a richer mixture is deposited, until

at a certain critical point the mixture or solution is entirely solid and consists of a homogeneous solution of the two constituents. Thus, in the case illustrated in fig. 24, a mixture of composition J, when cooled, begins to solidify at the temperature E, the first solid to be deposited having a composition shown by DI. The

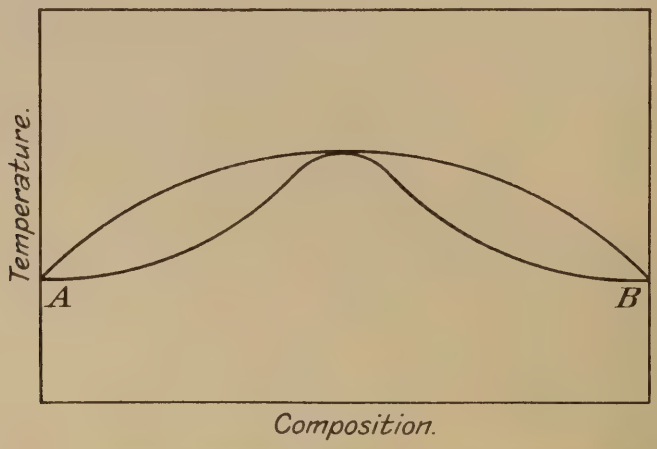


Fig. 25.—Phase Diagram of Miscible Liquids (with maximum point).

portion represented by I is solid, and the portion from I to J is liquid. As it cools further, the material becomes more solid and less liquid, the solid portion having a composition which approaches nearer and nearer to that of J, until, at the temperature L, its composition is shown by K and it is entirely solid. Conditions to the left of the line ADKFB give a solid phase and those to the right of ACHB give a liquid phase, whilst between the two lines is a mixture of solid and liquid.

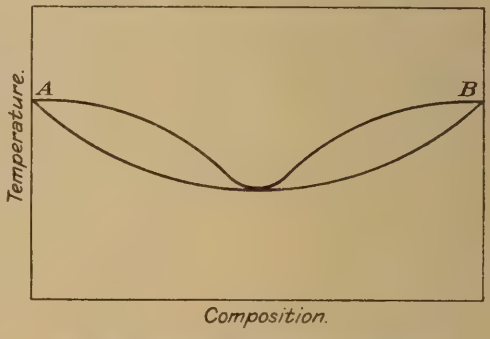


Fig. 26.—Phase Diagram of Miscible Liquids (with minimum point).

In some cases, two substances dissolve in each other in all proportions, but at one point the temperature and composition curves of each substance coincide and a substance with a composition corresponding to this point will show a sharp melting-point like a pure substance. The fusing-point of this substance may be higher or lower than that of either of the two pure substances forming the mixture. In fig. 25 there is a maximum melting-point at some point between the two extremes of composition, and at this point the solid solution phase has the same composition as the liquid phase. This type of graph is, however, extremely rare and it is doubtful whether it ever occurs in ceramic processes. Fig. 26 is similar, but instead of a maximum point it shows a minimum point which must not be confused with

an eutectic (*below*). Naturally, zoned crystals are probably associated by a curve of this type.

It is very difficult in some cases to decide to which of the last three types any binary mixture belongs, especially when the melting-point of the individual substances are very close to each other.

The form of continuous curve in which there is a transition-point is shown in fig. 27 ; it indicates the existence of two types of solid solutions or mixed crystals having an equilibrium point at K, compositions of the two types being shown by the points D and E. A natural example of this kind of diagram is shown by the pyroxenes (p. 415). Thus, if a mixture of silica, lime, and magnesia is heated, when the magnesia is in excess, enstatite ($MgOSiO_2$), an orthorhombic pyroxene, separates with very little calcium silicate ($CaOSiO_2$), but on cooling from the temperature K to B, the magnesia and lime unite with the silica, forming a monoclinic pyroxene, augite ($CaOMgO2SiO_2$). In this system, $CaOSiO_2$ is slightly soluble in $MgOSiO_2$, whilst $MgOSiO_2$ is very soluble in the augite series. The presence of other substances, such as iron oxide, may alter the order of crystallisation.

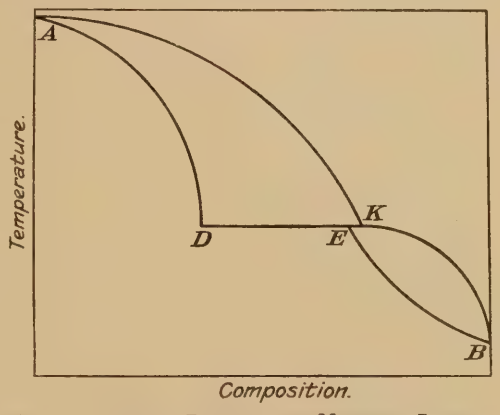


Fig. 27.—Phase Diagram of Miscible Liquids (with transition point).

Still more complex graphs are considered on p. 466 *et seq.*, but, in order to understand them better, it is necessary to consider the nature of eutectics.

An **Eutectic** is a substance of definite melting-point which may be higher or lower than that of the two substances from which the eutectic is produced. The existence of an eutectic is usually indicated by a sharp transition point in the equilibrium diagram graph of two or more substances. If the product corresponding to this transition-point is separated from the mixture it will usually be found to have a definite composition and a sharp melting-point—two important characteristics of a chemical compound. Some eutectics do not appear to consist of stable chemical compounds, but resemble a mechanical mixture of the substances concerned. The difference between a solid solution and an eutectic is that the former is a simple mixture, whilst the latter has a lattice-structure containing two or more sets of atoms and approaching a chemical compound in its properties. Thus, an eutectic is not a single-phase substance but a di- or poly-phase mixture.

Fig. 28 shows the temperature-composition curve of two substances, A and B, which form an eutectic, C. It will be seen that on cooling the fused mixture, the substance with the melting-point A, separates out along the line AC, and the substance B separates out along the line BC until the composition C is reached, when the mixture solidifies *en masse* as an eutectic. The transition-point C is sometimes termed the *eutectic-point*. In some cases, it is not merely a point but a straight line. Thus, when

water is cooled by freezing, the temperature remains at 0° C. until all the water is converted into ice.

If the time during which the cooling of a solution or fused mass is arrested by the formation of an eutectic is plotted against the composition of the mixture as a whole, a triangle will be obtained with its apex at the composition of the eutectic. From this it is possible to find the composition of any mixture of the same components at any temperature.

The formation of eutectics is very common in the preparation of metallic alloys ; it also occurs frequently in various ceramic processes, as will be described in detail later (p. 466).

In some cases, the graph or curve is complicated by two actions taking place

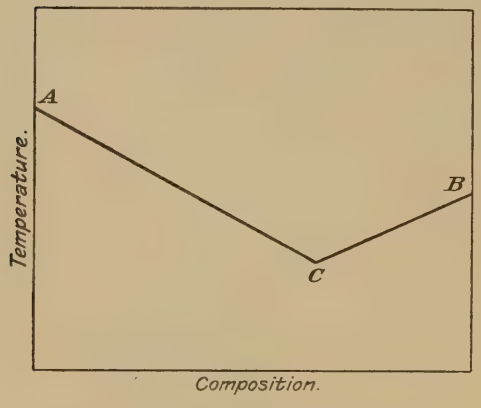


Fig. 28.—Eutectic Phase Diagram.

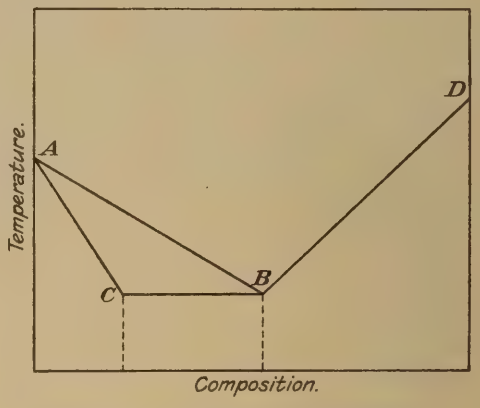


Fig. 29.—Solid Solution and Eutectic Phase Diagram.

simultaneously : (*a*) the formation, to a limited extent, of solid solutions, and (*b*) the formation of an eutectic. Thus, when two molten substances do not dissolve in each other in all proportions, the lines forming the graph corresponding to the composition of the solid deposited on cooling the fused mixture and the freezing-point do not meet, but appear as shown in fig. 29. In this diagram, a solid whose composition is represented by the line AC gradually separates out at temperatures AB, and at the temperature B an eutectic of composition B separates out.

Eutectics are not confined to two constituents, and in some cases ternary, quaternary, or even more complex eutectics are formed. They are much more difficult to investigate than the binary eutectics, and are sometimes very difficult to recognise, because in a highly complex liquid with a high viscosity no sharp eutectic-point is found. Under such conditions it is never easy to establish complete equilibrium, and, consequently, a liquid of high viscosity may cause erroneous conclusions to be reached.

An eutectic is usually recognised by a dip or depression in the graph of the equilibrium diagram, though this is not always the case. Hence, it is not necessarily correct to define an eutectic as a substance having the lowest melting-point in a series.

According to Vogt, the eutectic-point of two minerals is a mathematical function of their melting-points, latent heats, molecular weights, and electrolytic dissociation, but Doelter and some other investigators do not agree with this. Even if it is applicable to some mixtures, the number of cases where it is inapplicable make this theory of limited value.

The following summary of the work of Vogt and others on eutectics shows their normal behaviour :—

(*a*) Minerals having a high melting-point and a relatively high latent heat of fusion have an eutectic-point nearer to the more infusible mineral.

(*b*) Minerals which have a considerable difference in melting-points have an eutectic nearer to the more fusible mineral.

(*c*) Where the minerals have about equal melting-points the eutectic is approximately in the middle of the graph.

(*d*) Where the more fusible mineral has a higher molecular weight than the less fusible mineral the eutectic is nearer the more fusible mineral.

These statements must be modified as regards mixtures containing isomorphous crystals (p. 334) and where supersaturation occurs (p. 462), as in these cases and in some others, crystals sometimes separate in a different order from that which might be expected from a study of the phase diagram. Vogt has endeavoured to explain such irregular separation of minerals by means of a "common ion" theory by suggesting that the presence of a common ion in two or more components of a fused mass may cause the separation of a mineral containing it even when only a small amount is present. Thus, in a fused mixture containing felspar and spinel, the introduction of a ferro-magnesian mineral will cause the separation of spinel even though only 2 per cent. of the latter be present. Similarly, Harker has found that whilst in the ultrabasic rocks of the Isle of Rum, the olivine and anorthite have usually crystallised as anticipated forming an eutectic, yet when pyroxene was present the olivine always crystallised first.

When a common ion is present it appears to alter the eutectic composition and to displace the eutectic-point in a direction away from the mineral which has the higher fusing-point; by this means it accentuates the separation of minerals in inverse order of their fusibility. Such explanations based on the existence of a common ion only hold when the solutions are so dilute that their dissociation is complete and in the absence of complex reactions.

Apart from the abnormal cases, the composition of an eutectic may be calculated with considerable exactness from van't Hoff's law, which states that

$$d\mathrm{T} = 0{\cdot}0198\frac{\mathrm{T}^2}{\mathrm{L}},$$

where dT is the depression at the absolute temperature T and L is the latent heat of fusion per gram of solvent. The depression of the melting-point of a substance by the presence of another dissolved substance may also be expressed by the ratio MA$=k$, where M is the molecular weight of the solution and A is the depression of the freezing- or solidifying-point caused by a 1 per cent. solution. The reason that, when

several fluxes are present, their total effect is more powerful than that of an equal weight of any one of them, is because each flux causes a separate depression of the fusion-point, and, consequently, several fluxes reduce the fusion-point more than the presence of an equivalent amount of only one flux.

When some fused materials are cooled, no separation of the crystals of the eutectic occurs. This is attributed to the supersaturation of the molten material with some constituent which commences (and continues) to separate until the mixture has been cooled below the eutectic temperature; the extent to which the cooling can be carried beyond this point depends on the degree of supersaturation. Eventually a point is reached at which another constituent begins to separate rapidly, thus causing a rise in temperature, due to latent heat (which may amount to about 100 calories per gram). The separation of the second constituent continues until the remaining material has the same composition as the eutectic, after which the whole mass then crystallises in the form of an eutectic. The phenomena of supersaturation may produce abnormal effects in the order in which the crystallisation of different substances occur.

Definite Chemical Compounds.—In some cases, definite chemical reactions occur when molten liquids come into contact with each other and the resulting compounds may separate out in the form of almost pure crystals. Similar compounds are also formed when some mixtures are maintained at definite temperatures for a long time. The appearance of the phase diagram is somewhat different when compounds are formed from that produced when only mixtures are formed, as the solution of a pure substance in a compound or *vice versa* lowers the melting-point. Thus, a phase diagram in which compounds are formed shows a series of humps, according to the number of compounds formed, the summits of the humps representing the composition and melting-points of the compounds formed. The curve between any two humps resembles the graph in a simple phase diagram of two mixtures which do not form compounds, but have an eutectic composition or form solid solutions.

A definite chemical compound differs from a solid solution in that the former has a sharp melting-point, whilst solid solutions have a fusion range. Some highly refractory substances have so low a thermal conductivity, however, that unless the fusion of a few minute grains is observed under the microscope, a definite compound, such as quartz, may appear to have a fusion range and so be mistaken for a solid solution. On the other hand, Ludwig's hypothesis, that fireclay bricks are solid solutions of "impurities" in the pure clay, enables the melting-points of many clays to be calculated from their chemical composition (see p. 382).

The formation of compounds prior to fusion often has a very important effect on the temperature at which the fusion occurs. Thus, litharge attacks silica at a temperature of about 700° C., although its melting-point is 200° C. higher, and that of silica is about 1600° C. Similarly, the surface of crystalline potash felspar becomes "soft" about 200° C. below the fusing-point of that mineral. Cobb has shown that lime and silica can combine very extensively, forming calcium silicate at about 800° C.—a temperature much below the fusion-point of the product.

This formation of compounds—some of which may fuse at a higher temperature

than that at which they are produced—plays a very important part in the production of vitrified ware (see Chapter XIII.).

Complex Fusion Curves.—The fusion curves of many binary mixtures are not so simple as those which have been described in the preceding pages, but involve many other phenomena. Thus, the fused mass after cooling slowly may contain chemical compounds, eutectics, and solid solutions.

In a *ternary system*, in which more than two substances are present in the molten mass, the phase diagram cannot be plotted in a single plane, but takes the form of a

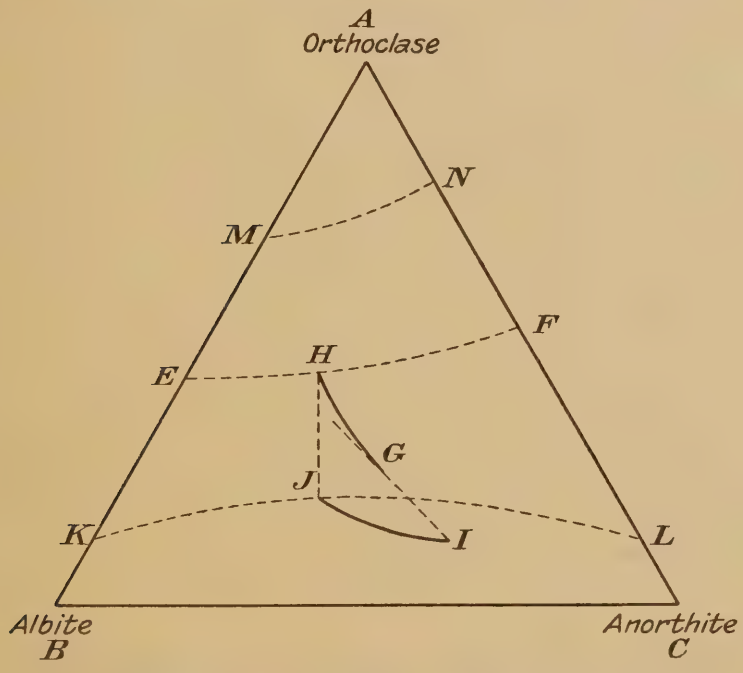


FIG. 30.—TERNARY PHASE DIAGRAM OF ORTHOCLASE-ALBITE-ANORTHITE SYSTEM.

triangular diagram, as shown in fig. 30, where A, B, and C represent 100 parts of each of their constituents. If E is the eutectic-point of A—B, and F the eutectic-point of A—C, whilst the substances corresponding to B—C are completely miscible, the composition of any melt and the crystals separating from it may be plotted. Thus, if the composition changes from G—H and the mixed crystals from I—J, when the curve GH touches the curve EF, a tangent to the curve GH from H cutting the curve IJ will give a point which corresponds to the limit of mixed crystals of the system BC in A. By examining the compositions of various mixtures, the curves KL and MN may be developed. The former is the limit of solubility of BC in A, whilst the latter is the limit of solubility of A in BC. The simplest form of ternary system is one in which no compounds or solid solutions are formed, but only one eutectic point. Where the three substances, taken in pairs, form eutectics with each other, the

corresponding phase diagram is similar to that shown in fig. 31. Such a system has four eutectic-points, namely, the binary eutectic points, because

A—B has a eutectic D
A—C „ „ E
B—C „ „ F

and I is the ternary eutectic-point, which is the eutectic characteristic of the system as a whole.

A *quarternary system* would require a phase diagram of four dimensions, so that

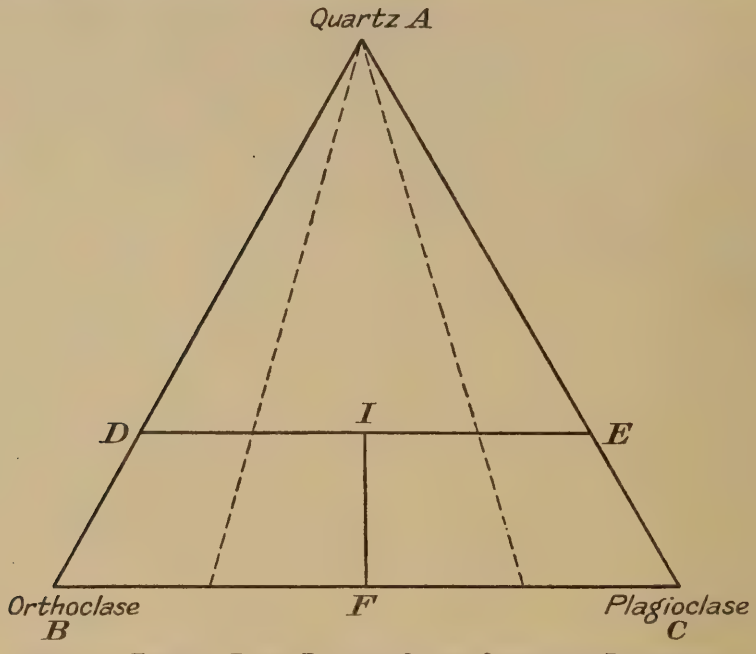


Fig. 31.—Ternary Phase Diagram Quartz-Orthoclase-Plagioclase System.

it is almost impossible to express graphically on paper the reactions which occur in such a system ; a model in the form of a solid tetrahedron may be prepared which will show these changes.

Time-Temperature Curves

In accordance with Gibbs' phase rule (p. 453), if both time and temperature are stipulated and there are two components in the system, V=2 and C=2, so that

$$P+2=2+2,$$

i.e. P=2, so that two phases are possible. In dealing with ceramic materials these will usually be the liquid and solid phases. Whether any liquid material is produced depends on whether the temperature is sufficiently great. This must be ascertained by actual investigation of the products at different temperatures or after different

intervals of time. On the other hand, if there is only one component and two conditions V=2, C=1, and

$$P+2=1+2,$$

so that P=1 and there can only be one phase. In the former case, the temperature-composition diagram can be made to show under which of these conditions the solid and liquid phases can exist either separately or simultaneously, whilst in the latter case only one phase is possible. For some purposes, however, there is no need to ascertain the nature and number of the phases, and a simple time-temperature graph will then suffice. Such a diagram is often very useful for showing the rate at which a substance can be heated when heat is supplied to it externally at a constant rate. Where no change occurs in the rate of heating, the graph would take the form of a straight line or a regular and unbroken curve. If, however, any physical or chemical change occurs in the material this will be shown by some irregularity or change in the direction of the curve indicating a transition-point. Hence, a time-temperature curve of the heating or cooling of some materials is of great value and shows when changes begin to take place in them. Thus, the cooling curve shown in fig. 32 shows that a change begins to occur at a temperature G° and continues to E° when another change occurs, as a result of which the temperature remains constant for a time represented by the horizontal portion of the curve, after which the cooling continues uniformly with no further change in state. A comparison of temperature-composition and time-temperature curves is very interesting and instructive. Thus, fig. 33 shows these two curves, the right-hand portion showing the time-temperature curve of a material of a composition indicated by the vertical line.

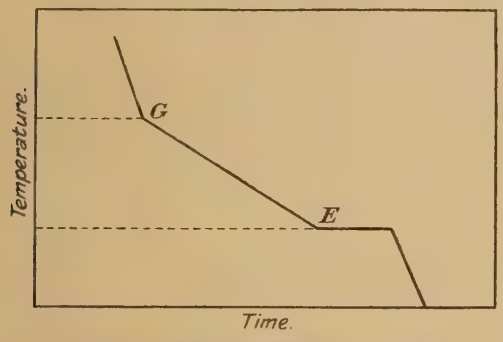


FIG. 32.—TIME-TEMPERATURE CURVE.

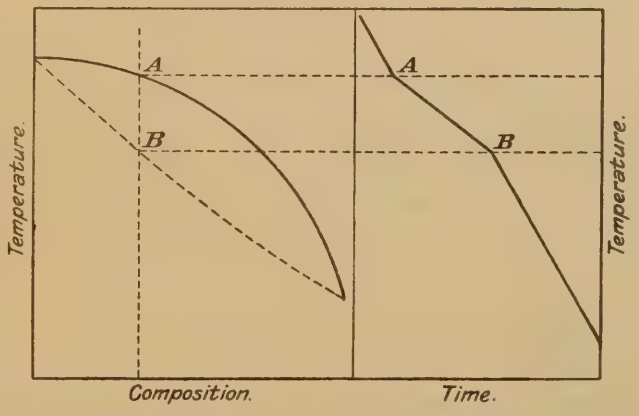


FIG. 33.—TEMPERATURE-COMPOSITION AND TIME-TEMPERATURE CURVES.

From these two curves it will be seen that the range of temperature during which solidification occurs, as shown by the temperature-composition graph, coincides with the irregularity in the time-temperature graph.

Time-temperature curves are also useful in determining the quantitative results of any reaction. Thus, in the formation of eutectics, the time taken in a given apparatus to form the eutectic is directly proportional to the amount of eutectic formed, so that by estimating the time during which no cooling occurs, the amount of eutectic which can be formed may be found. Time-temperature curves are also very useful in connection with the study of crystallisation (p. 489).

These applications of graphs are dealt with more fully in the next section.

In considering the cooling-curves of substances, it must be remembered that the effect of supercooling (p. 487) may conceal any small critical point or range on the curve. A heating curve is often more reliable than a cooling one, as the effects are not so pronounced and minor critical points are less liable to escape detection.

PHASE CONDITIONS IN CERAMIC PROCESSES

The reactions occurring during the heating or " burning " of various materials used in the ceramic industries are very complex, and in order to obtain even a partial conception of them it is necessary to understand what occurs in the case of some of the simpler systems ; from a comparison of these, a considerable amount of information respecting the more complex systems may be obtained.

Binary Systems

Binary systems of interest to students of ceramics chiefly consist of a base (usually a metallic oxide) and an acid (usually silica), but other binary systems in which both components are metallic oxides must also be considered. The binary systems vary greatly in stability, some of them being readily decomposed, whilst others are highly stable. This characteristic cannot be predicted with certainty from their composition, though the more stable binary compounds are usually those in which the molecular ratio most nearly approaches unity. Thus $3CaO\ SiO_2$, with a ratio of 3 : 1, is much less stable than $CaO\ SiO_2$, with a ratio of 1 : 1.

Binary systems consisting of a base and silica may form definite chemical compounds, solid solutions or eutectics according to their components. Binary silicates are usually formed at a temperature about 200° C. above their fusing-point, though this should not be taken as a fixed rule, as the difference between the temperature of formation and the fusing-point is not always constant and Cobb has shown that lime can combine with silica at a temperature much below the fusing-point of either of these oxides and also below that of their product. Singulo-silicates usually form at lower temperatures than those having a higher oxygen ratio. Sub-silicates, which are more basic, and bi- and tri-silicates, which are more siliceous, are usually formed at higher temperatures. Thus, if a bisilicate consisting of $RO\ SiO_2$ comes into contact with a basic material, it tends to produce a substance having the formula $2RO\ SiO_2$, but if it originally corresponded to $4RO\ SiO_2$ it would tend to combine with silica and to form $2RO\ SiO_2$. Silicates with only one base have a lower refractoriness than the materials from which they are formed, thus :

	CaO.	SiO_2.	$CaOSiO_2$.
Fusing-point . .	1900° C.	1850° C.	1512° C.

	MgO	SiO_2.	$MgOSiO_2$.
Fusing-point . .	2000° C.	1850° C.	1524° C.

Silicates with more than one base fuse at lower temperatures than those with only one, in accordance with van't Hoff's Law (p. 461). Similarly, mixtures of silicates have a lower fusing-point than the same silicates when heated separately; thus, 70 parts of $CaOSiO_2$, fusing at 1512° C., and 30 parts of $MgOSiO_2$, fusing at 1524° C., form an eutectic which fuses at 1350° C.

The **lime-silica system** has been examined in detail by Day and Shepherd,[1] who found three eutectic-points as follows :—

1. At a temperature of 1417° C. an eutectic mixture consisting of tridymite and pseudo-wollastonite is formed.

2. At 1480° C. an eutectic consisting of pseudo-wollastonite and a lime-olivine is formed.

3. At 2015° C. an eutectic of lime olivine and lime is formed.

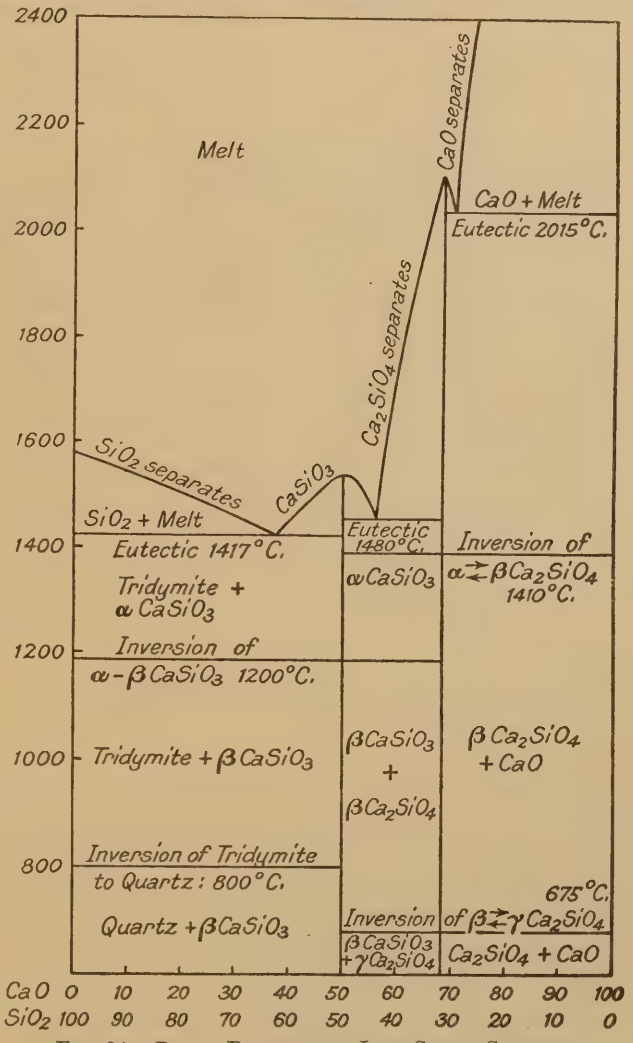


FIG. 34.—PHASE DIAGRAM OF LIME-SILICA SYSTEM. (DAY AND SHEPHERD.)

Two definite compounds are shown in the equilibrium diagram (fig. 34), namely, calcium orthosilicate ($2CaO\ SiO_2$) which melts at 2130° C., and calcium metasilicate ($CaO\ SiO_2$) which melts at 1540° C. J. Cobb found that the orthosilicate is formed unless there is a large excess of silica present, in which case the metasilicate may be formed.

[1] *Amer. J. Sci.*, **22**, 265 (1906).

Calcium orthosilicate exists in three forms :

a. Stable above 1410° C.—monoclinic ; specific gravity 3·27 ; hardness, 5–6.
β. Stable 1410°–675° C.—orthorhombic ; specific gravity 3·28.
γ. Stable below 675° C. ; monoclinic specific gravity 2·97.

Calcium metasilicate (wollastonite) exists in two forms :

a. Stable between 1512° C. and the melting-point.
β. Stable up to 1512° C.

According to Boudouard, the metasilicate is the most fusible silicate of lime.

It must be clearly understood that an equilibrium diagram obtained from observations on the cooling of a fused material will not necessarily show the lowest temperatures at which the compounds indicated can be formed. When such compounds are formed by gradually heating their component oxides, the temperature at which the latter interact depends on the intimacy of association (p. 445) and the allotropic form of the substances, as well as on the other factors mentioned on pp. 437–449. An equilibrium diagram for cooling may lead to erroneous conclusions if it is assumed to be applicable in the reverse direction to that on which the observations were based.

Calcium silicates may, according to Cobb, be formed at as low a temperature as 800° C., if they are in intimate contact, the action taking place below the melting-point of the eutectic without any signs of fusion. Hedvall found that quartz and cristobalite begin to react with lime at about 1400° C., the latter being more resistant than the former. Quartz-glass, at 1000° C., reacts rather feebly with lime, but precipitated silica is rapidly attacked.

The **soda-silica system** includes two compounds, sodium metasilicate (Na_2OSiO_2) and sodium tetrasilicate (Na_2O4SiO_2) ; the latter appears to be the chief constituent of water-glass. When silica is heated with common salt (sodium chloride) in the presence of water-vapour, as in salt glazing, combination occurs as shown in the equation :—

$$SiO_2+2NaCl+H_2O=Na_2OSiO_2+2HCl.$$

The **magnesia-silica system** includes two compounds, which are, according to Allen and Wright : (*a*) $MgOSiO_2$ (m.-pt. 1554° C.), (*b*) $2MgOSiO_2$ (m.-pt. over 1750° C.), which is identical with the mineral *forsterite*. It is also produced when magnesia bricks containing silica as an impurity are maintained for some time at a temperature above 1500° C. In some cases, as has been noted by Kowalke and Hongen, forsterite crystals may completely surround periclase (MgO) crystals, thus producing a very strong bond, and, for this reason, the presence of 5 per cent. of silica is considered desirable by many Continental users of magnesia bricks.

The magnesia-silica system is particularly difficult to investigate as the products are so highly viscous that there is always some uncertainty as to whether a state

of equilibrium has been reached. Fig. 35 shows the equilibrium diagram of the MgO–SiO_2 system, according to Sosman.[1]

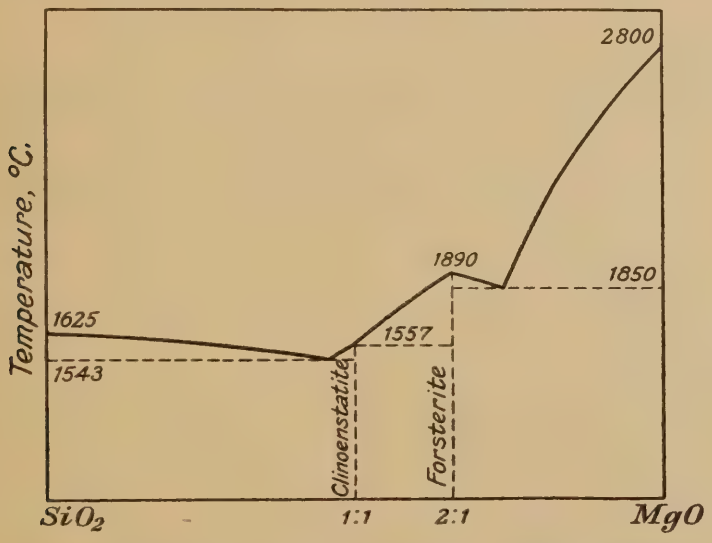


FIG. 35.—PHASE DIAGRAM OF MAGNESIA-SILICA SYSTEM. (SOSMAN.)

The **barium oxide-silica system** includes, according to P. Eskola,[2] the following compounds and eutectics :—

Compounds :—

(*a*) $2BaOSiO_2$.
(*b*) $BaOSiO_2$ (m.-pt. 1604° C.).
(*c*) $2BaO\ 3SiO_2$ (m.-pt. 1450° C.).
(*d*) $BaO\ 2SiO_2$ (m.-pt. 1420° C.).

Eutectics :—

(*a*) $2BaOSiO_2$ and $BaOSiO_2$ (m.-pt. 1557° C.).
(*b*) $BaOSiO_2$ and $2BaO3SiO_2$ (m.-pt. 1437° C.).
(*c*) $BaO\ 2SiO_2$ and SiO_2 (m.-pt. 1374° C.).

In addition to the foregoing, mixtures of $2BaO3SiO_2$ and $BaO2SiO_2$ form a continuous series of solid solids containing these components in any proportions.

The **strontia-silica system** includes, according to P. Eskola,[2] the following compounds and eutectics :—

Compounds :—

(*a*) $2SrOSiO_2$ (m.-pt. above range of electric furnace).[3]
(*b*) $SrOSiO_2$ (m.-pt. 1578° C.).

Eutectics :—

(*a*) $2SrOSiO_2$ and $SrOSiO_2$ (m.-pt. 1545° C.).
(*b*) $SrOSiO_2$ and SiO_2 (m.-pt. 1358° C.).

[1] *Trans. Faraday Soc.*, **12**, 170 (1917). [2] *Amer. J. Sci.*, **4**, 331–75 (1922).
[3] According to Jaeger and Van Klooster [*Sprechsaal*, **52**, 256 (1919)] it is above 1750° C.

The **zinc oxide-silica system** includes the following definite compounds :—

$ZnOSiO_2$ (m.-pt. 1437°±1° C.),[1]
$2ZnOSiO_2$ (m.-pt. 1509·5°±0·5° C.) ; [1]

the latter is identical with the mineral *willemite*.

The **manganese oxide-silica system.**—Manganese oxide and silica produce orthosilicates and metasilicates :

$2MnOSiO_2$ (m.-pt. 1290°–1300° C.) [1] is identical with the mineral tephroite. Artificial tephroite has no definite melting-point, but darkens on heating and decomposes before melting completely.

$MnOSiO_2$ (m.-pt. 1273°±1° C.) [1] is identical with the mineral *rhodonite*, which melts between 1221° and 1270° C.).[1]

Tephroite forms solid solutions with fayalite ($2FeOSiO_2$), but whilst rhodonite may take some iron into solution, it does not appear to form a definite metasilicate.

The **iron oxide-silica systems** are complicated by the existence of three iron oxides (p. 418) and by the comparative ease with which the red ferric oxide and the black magnetic oxide can be reduced and form the dark ferrous oxide.

Ferrous oxide reacts with silica, forming *fayalite* ($2FeOSiO_2$), and *grünerite* ($FeOSiO_2$). The former forms solid solutions with tephroite ($2MnOSiO_2$), and also with forsterite ($2MgOSiO_2$).

Very little is known of the iron oxide-silica systems, although they play a highly important part in the production of vitrified materials, especially in the manufacture of blue bricks. They are also important in the manufacture of silica bricks, but the latter are simpler, because in them most of the iron is in the form of fayalite, though free magnetite occurs in some bricks.

The **zirconia-silica system** includes only one eutectic, which is identical with the mineral zircon $ZrSiO_4$, with a fusing-point, according to Washburn and Libman,[2] of 2300° C., which is intermediate between that of zirconia (ZrO_2), viz. 2700° C.[2] and silica (SiO_2), viz. 1470° C.

If zirconia and zircon are heated they appear to form a eutectic having a fusing-point of about 2300° C., which is the same as that of the zircon and is probably identical with it. In that case there is no true eutectic, as this term cannot be applied to either of the components of the system, but only to an intermediate substance containing both components.

The **lime-alumina system** includes various calcium aluminates which are much more fusible than either lime or alumina.

Free lime and alumina begin to interact between 800° C. and 900° C. ; the reaction becomes very rapid as 1100° C. is approached and, according to Cobb, is practically complete at 1300° C. The chief calcium aluminates which are found in burned clays are :

$5CaO\,3Al_2O_3$ (m.-pt. 1386° C.),
$3CaOAl_2O_3$ (found at 1530° C.).

---

[1] Jaeger and Van Klooster.

[2] *J. Amer. Cer. Soc.*, **3**, 634 (1920).

Rankin and Wright state that the following compounds may also be formed :—

$$CaOAl_2O_3$$
$$3CaO5Al_2O_3;$$

they are not found in burned clays. $CaO2Al_2O_3$ may be formed at temperatures below 1100° C., but above this temperature a compound richer in alumina is found which is insoluble in hydrochloric acid in the cold, whilst the more calcareous compound is completely soluble. The phase diagram of alumina and lime is shown in fig. 36, due to Sosman.[1]

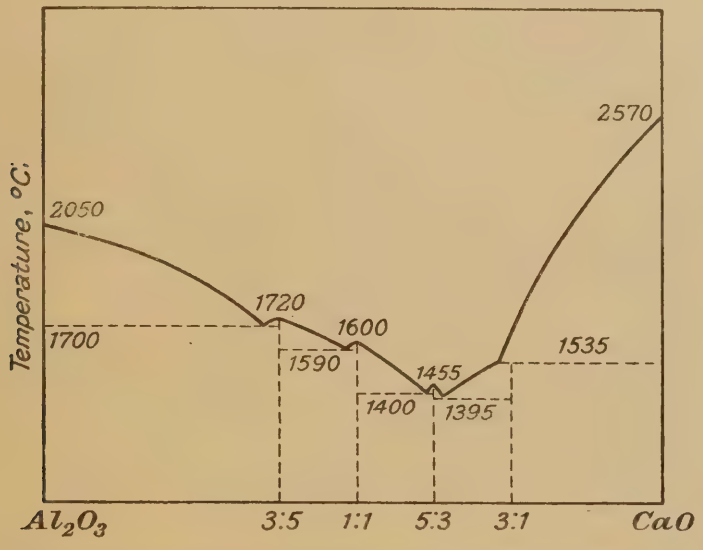


Fig. 36.—Phase Diagram of Lime-Alumina System. (Sosman.)

The **magnesia-alumina system** yields one compound—spinel ($MgOAl_2O_3$), with a melting-point of 2135° C. The phase diagram is shown in fig. 37.

The **iron oxide-alumina system** like the corresponding silica system is complicated by the existence of three iron oxides (p. 418). So far as the ferrous oxide-alumina system is concerned the chief compound is *hercynite* ($FeOAl_2O_3$). The iron-alumina systems have not, however, been fully investigated.

The **iron oxide-lime system** is complicated like the corresponding ones containing alumina and silica respectively. When lime and iron oxide are heated together ferrates may be formed. The two chief compounds are calcium metaferrate ($CaOFe_2O_3$), which melts at 1205° C., and, according to Sosman and Merwin, dissociates at the same temperature, forming long, black, needle-shaped crystals, whilst the second compound calcium orthoferrate ($2CaOFe_2O_3$) melts at 1400° C. and almost immediately dissociates, forming black crystals having a yellowish brown tinge by reflected light. The phase diagram, due to Sosman,[1] is shown in fig. 40.

[1] *Loc. cit.*, p. 469.

Very little calcium meta- or ortho-ferrate is formed when clays are burned as the proportion of iron oxide is not usually sufficient.

The **silica-alumina system** has been investigated by Shepherd and Rankin,[1] who found two eutectics, one (m.-pt. 1800° C.) containing just over 50 per cent. of silica and the other (m.-pt. about 1580° C.) containing about 6 per cent. of silica.

When clays are heated to about 1300° C., sillimanite ($Al_2O_3SiO_2$) is gradually formed to an extent depending on the duration of the heating. As the temperature increases, the rate at which sillimanite forms also increases, a rise of temperature acting in the same way as a prolongation of the time of heating.

Seger in 1893 published data (fig. 38) showing the refractoriness of a series of

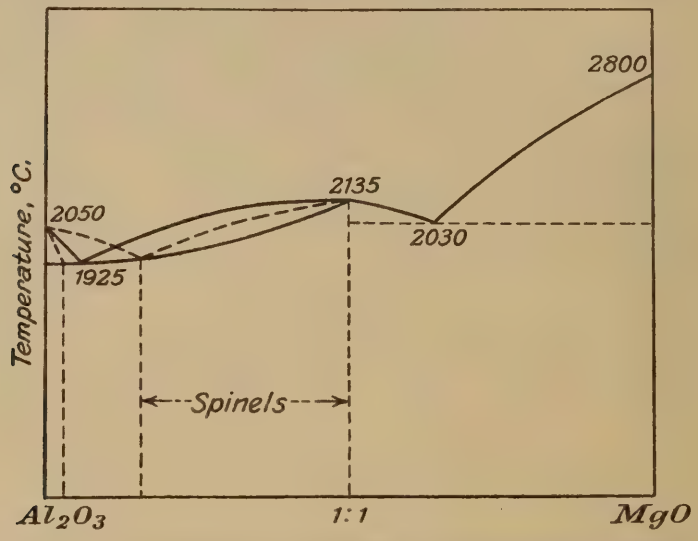


FIG. 37.—PHASE DIAGRAM OF MAGNESIA-ALUMINA SYSTEM. (SOSMAN.)

mixtures of silica and alumina. The conditions of his experiment were not such as to produce a sharply defined eutectic, but the transition-point at or near a composition corresponding to $Al_2O_317SiO_2$ is very noticeable. It is also interesting to note that such an artificial mixture of alumina and silica has the same composition as some of the best ganisters, because ganister has long been prized commercially for its resistance to heat, whilst, according to Seger, it is more fusible than any other mixture of alumina and silica. The difference may be partly, though not wholly, explained by the fact that Seger used extremely finely-ground alumina and silica, whereas ganister is composed of coarser grains. Fig. 38 also shows the importance of using either pure silica or pure alumina where a heat-resisting material is required as the loss in refractoriness with even a small proportion of impurity is very great.

Fig. 39 shows the phase diagram of the alumina-silica system, according to Sosman.[2]

The **silica-sillimanite system** may be regarded as a portion of the silica-alumina

[1] *Amer. J. Sci.*, **27**, 302 (1909). [2] *Loc. cit.*, p. 469.

system, but in view of the importance of sillimanite in the ceramic industries it is convenient to consider it separately. Cristobalite and sillimanite and also sillimanite and alumina form eutectics, but do not dissolve each other to any appreciable extent

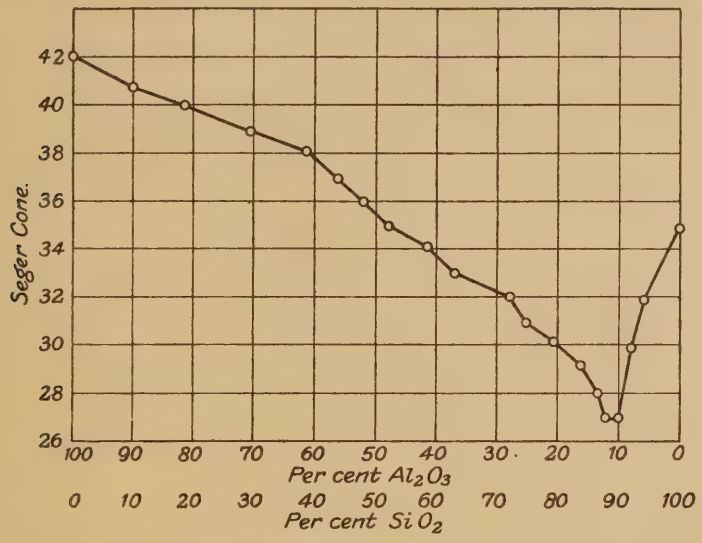


FIG. 38.—FUSION CURVE OF ALUMINA-SILICA MIXTURES. (SEGER.)

so as to form solid solutions. According to Rankin and Wright,[1] the eutectic composition is 87 parts of silica and 13 parts of alumina, which is equivalent to

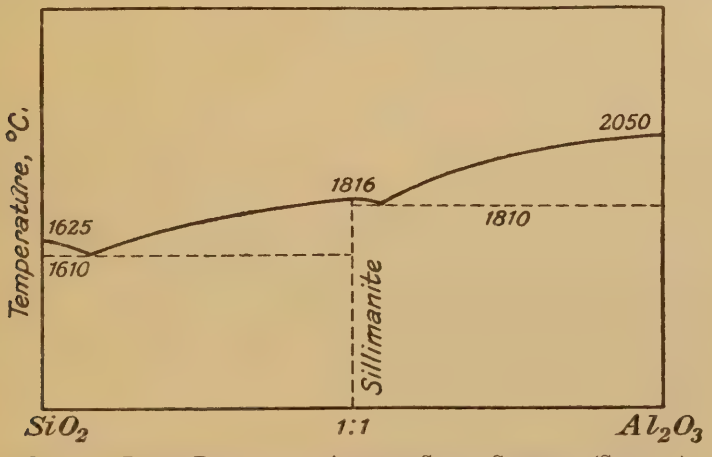


FIG. 39.—PHASE DIAGRAM OF ALUMINA-SILICA SYSTEM. (SOSMAN.)

approximately 79 parts of silica and 21 parts of sillimanite. This fuses at 1610° C. and corresponds very closely in composition to Seger Cone 28, which has a refractoriness of 1630° C.

[1] *Amer. J. Sci.*, **39**, 9 (1915).

The **iron oxide-magnesia system** has not been fully investigated. It is known that ferrous oxide enters into solid solution in magnesia to a limited extent and that ferric oxide may combine with magnesia to form magnesio-ferrite ($MgOFe_2O_3$). This substance also forms mixed crystals with magnesia. It has been detected in magnesia bricks by Cornu and Cronshaw independently.

Both ferric and ferrous oxide rapidly react with magnesia. For this reason magnesia bricks should not usually be heated in contact with very hot iron oxide. In what are known as " Metalkase bricks," which are iron cylinders packed with dead-burned magnesia, use is made of the reaction of these two substances to form a magnesic mass with a very strong bond.

Ternary Systems

When three substances are heated together the number of compounds which can be produced is greatly increased. Such systems are of considerable importance in the ceramic industries, though few of them have been investigated. The ternary systems may conveniently be divided into two groups :

(*a*) Base-base-silica systems.
(*b*) Base-alumina-silica systems.

This subdivision is desirable because alumina behaves abnormally, acting sometimes as a base (in which case systems containing it may be included in the first of the above groups) and sometimes acting with the silica to form a complex acid (alumino-silicic acid), and so causing the systems in which it so acts to behave almost as binary systems.

BASE-BASE-SILICA SYSTEMS

The **lime-magnesia-silica system** is very complex ; according to Ferguson and Merwin,[1] there are fourteen crystalline phases in this ternary system, the triangular equilibrium diagram showing fourteen invariant points at which three crystalline phases and a liquid phase can coexist, and, of these, six are eutectics. Besides these, there are five series of solid solutions.

Ferguson and Merwin found that the most fusible (eutectic) mixture contains 32 per cent. of lime, 7 per cent. of magnesia, and 61 per cent. of silica, which does not correspond to any definite chemical formula ; it melts at 1320° C.

Two well-known substances found in this system occur in Nature as *diopside* ($CaOMgO2SiO_2$ (m.-pt. 1391° C.)) and *monticellite* ($2CaO2MgO2SiO_2$), a material similar to which has been found by A. Scott in some British magnesia bricks. Fig. 41 shows a triangular diagram of the lime-magnesia-silica system prepared by Ferguson and Merwin.

The **lime-barium oxide-silica system** has only been partly investigated ;

[1] *Amer. J. Sci.*, 48, 6 (Fourth Series) (1919).

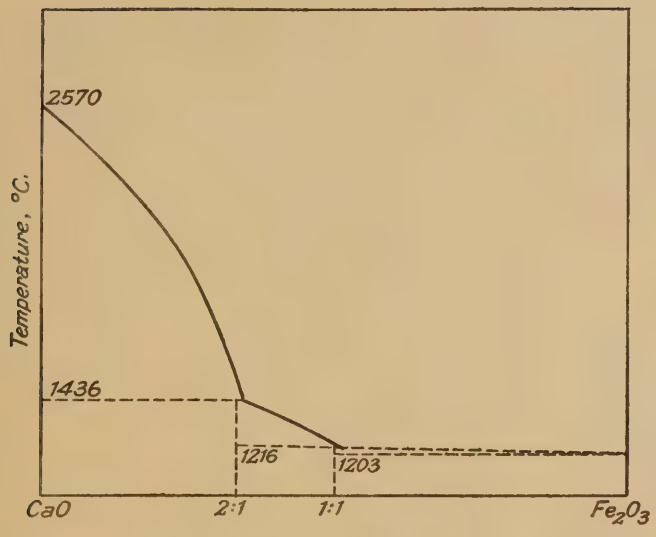


FIG. 40.—PHASE DIAGRAM OF LIME-FERRIC OXIDE SYSTEM.
(SOSMAN.)

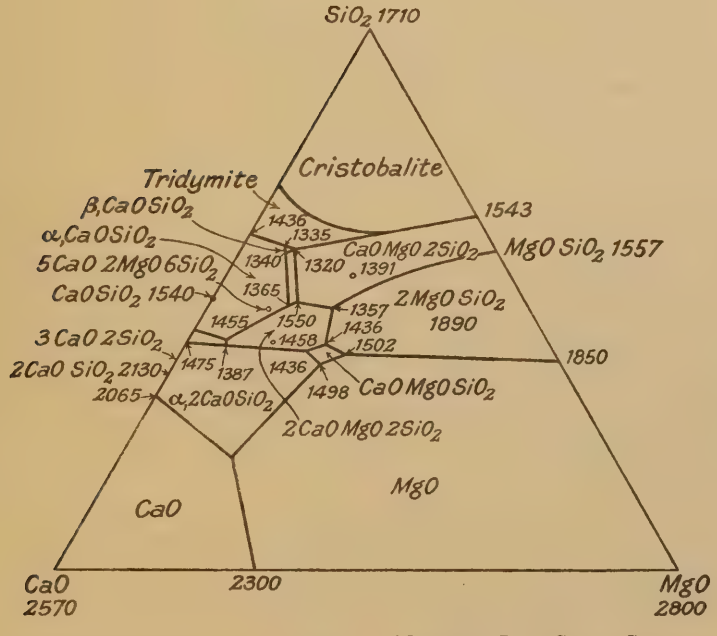


FIG. 41.—TRIANGULAR DIAGRAM OF MAGNESIA-LIME-SILICA SYSTEM.
(FERGUSON AND MERWIN.)

according to P. Eskola,[1] fused calcium and barium silicates cannot remain mixed in indefinite proportions; on cooling, $2CaOBaO3SiO_2$, which is infusible, forms but dissociates, yielding α-$CaOSiO_2$ and a liquid whose composition has not been determined.

In the **lime-lithia-silica system,** when prepared by fusing lithium and calcium silicates, are two series of mixed crystals and an eutectic (melting-point 979° C.) containing 50 per cent. of calcium silicate.

The **lime-strontia-silica system,** according to P. Eskola,[1] forms a continuous series of solid solutions with a minimum melting-point at 1474° C.±3°. An analysis

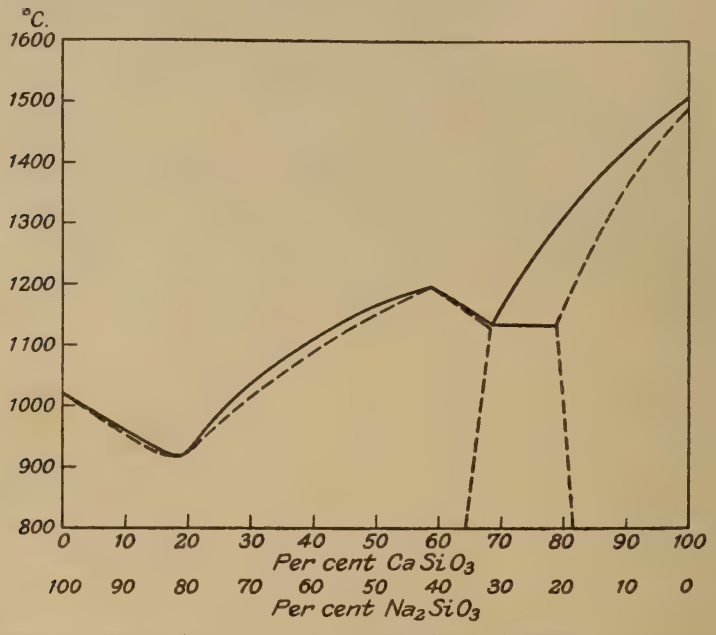


Fig. 42.—Phase Diagram of Soda-Lime--Silica System. (Wallace.)

of this substance shows that it contains 44 per cent. calcium silicate ($CaOSiO_2$) and 56 per cent. strontium silicate ($SrOSiO_2$).

The **soda-lime-silica system** (fig. 42), when prepared from sodium and calcium silicates, includes, according to Wallace,[2] two series of mixed crystals with an eutectic (melting-point 1140° C.) containing 70 per cent. $CaSiO_3$. The curve between 0 and 70 per cent. $CaSiO_3$ shows a maximum at 58·8 $CaSiO_3$ corresponding to the formula $2Na_2SiO_33CaSiO_3$, and a minimum at 20 per cent. $CaSiO_3$ which does not correspond to any definite formula.

The **soda-lithia-silica system,** according to Wallace,[2] forms an unbroken series of mixed crystals, with a minimum fusing-point at 40 per cent. Li_2SiO_3.

The parts of the **soda-magnesia-silica system,** which contained 0–10 per cent. and 90–100 per cent. of magnesium silicate, were found by Wallace[2] to consist of mixed

[1] *Loc. cit.*, p. 469.

[2] *Trans. Eng. Cer. Soc.*, 9, 175 (1909–10).

crystals of sodium and magnesium silicates ; the material containing between 20 and 80 per cent. of magnesium silicate is a glass.

The **soda-strontia-silica system,** prepared from sodium and strontium silicates, consists, according to Wallace,[1] of an unbroken series of mixed crystals, those with a minimum fusing-point corresponding to a mixture containing 20 per cent. by weight of strontium silicate and 80 per cent. of sodium silicate, corresponding approximately to $SrSiO_3 5{\cdot}36Na_2SiO_3$.

In the **potash-lithia-silica system** Wallace [1] found that mixtures of potassium silicate and lithium silicate containing more than 60 per cent. of lithium silicate

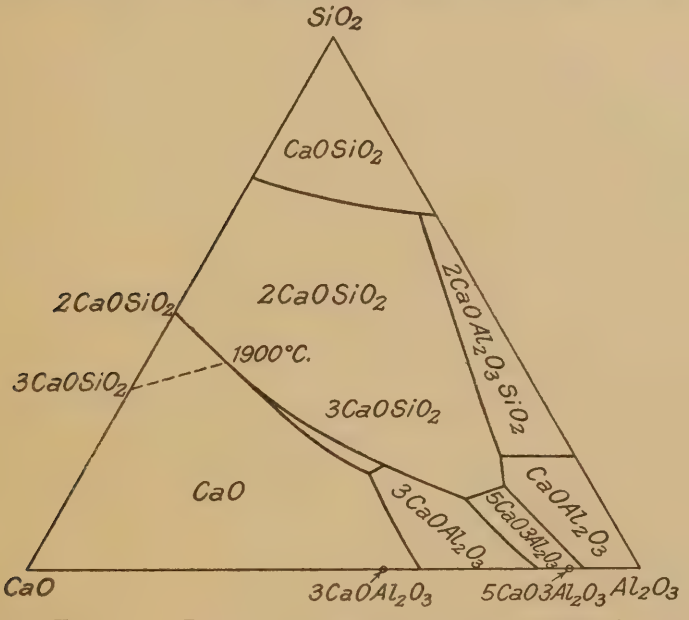


Fig. 43.—Triangular Diagram of Lime-Alumina-Silica System.[2] (Little.)

produce an unbroken series of mixed crystals. Mixtures of these two silicates containing less than 50 per cent. of lithium silicate are glasses which exhibit no signs of any crystallisation.

The **barium oxide-soda-silica system,** when prepared from barium and sodium silicates, forms, according to Wallace,[1] an unbroken series of mixed crystals. The portion with a minimum fusing-point contains 40 per cent. of barium silicate and corresponds approximately to $BaSiO_3 2{\cdot}64Na_2SiO_3$.

The **barium oxide-lithia-silica system,** obtained by fusing lithium and barium silicates, according to Wallace,[1] shows two series of mixed crystals and one eutectic (melting-point 880° C.) containing 78 per cent. of barium silicate ($BaSiO_3$).

The **magnesia-lithia-silica system** obtained by fusing lithium and magnesium silicates, according to Wallace,[1] shows two series of mixed crystals and one eutectic (melting-point 876° C.) containing 55 per cent. of magnesium silicate ($MgSiO_3$).

[1] *Loc. cit.*, p. 477.

[2] *Textbook of Inorganic Chemistry*, 4, 78 (Griffin).

The **lithia-strontia-silica system,** prepared from lithium and strontium silicates, forms two series of mixed crystals, according to Wallace,[1] with one eutectic (melting-point 1000° C.) containing 60 per cent. of strontium silicate.

In the **iron oxide-magnesia-silica system** the binary compounds, *forsterite* ($2MgOSiO_2$) and *fayalite* ($2FeOSiO_2$), form solid solutions in which each of these silicates are miscible in all proportions.

BASE-ALUMINA-SILICA SYSTEMS

A very important class of reactions which take place in ceramic processes includes

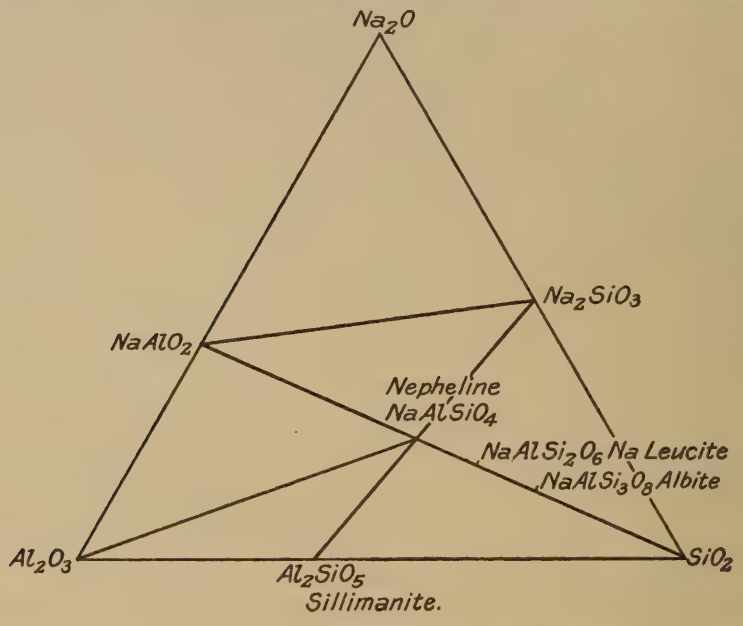


FIG. 44.—TRIANGULAR DIAGRAM OF SODA-ALUMINA-SILICA SYSTEM. (WALLACE.)

those in which alumina and silica are present together with one or more bases. The abnormal behaviour of alumina in such substances has been explained on p. 474. As a result of this behaviour, the effect of fluxes on such systems depends upon various factors, including the nature and amount of base, and to some extent on the relative proportions of alumina and silica. In the latter connection it should be observed that Montgomery and Fulton [2] found that the maximum effect of the fluxes is obtained with a silica : alumina ratio between 7 : 1 and 5 : 1.

The **lime-alumina-silica system** (fig. 43), prepared by fusing calcium metasilicate ($CaSiO_3$) and sillimanite (Al_2SiO_5), shows two eutectic points—one at 1300° C., consisting of calcium silicate and anorthite, and one at just above 1500° C., consisting of anorthite and sillimanite. The system contains one ternary compound (anorthite),

[1] *Loc. cit.*, p. 476.

[2] *Trans. Amer. Cer. Soc.*, **19**, 303 (1917).

which is formed at about 1540° C. and corresponds to equal parts of calcium silicate and sillimanite. The mineral gehlenite ($2CaOAl_2O_3SiO_2$) does not appear in the phase diagram of this system, so that it is not, apparently, a ternary compound, but a solid solution.

Owing to the abnormal behaviour of alumina in ternary systems, the ratio of the other metallic oxide (base) present is often of great importance and often seems to determine the behaviour of the alumina. This appears to particularly be the case in a ternary system composed of lime, alumina, and silica. Thus, according to G. Rigg, when a slag composed almost wholly of $2CaOSiO_2$ dissolves 19·6 per cent. of alumina, the fusing-point rises from 1382° C. to 1453° C., but the solution of a

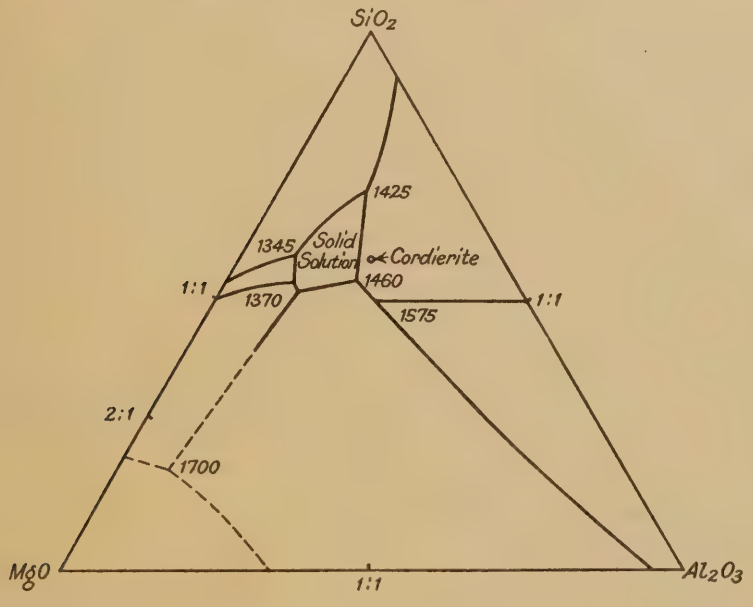


Fig. 45.—Triangular Diagram of Magnesia-Alumina-Silica System. (Sosman.)

similar proportion of alumina by a slag consisting chiefly of $CaOSiO_2$ reduces the fusing-point from 1460° C. to 1272° C. Again, G. A. Rankin has stated that when clay and an excess of lime are heated, the product first formed corresponds to $5CaO3Al_2O_3$ and the succeeding product to $2CaOSiO_2$, both these compounds absorbing lime as the temperature increases. He found that, at 1335° C., the fluid mass consists of $2CaOSiO_2$, $5CaO3Al_2O_3$, and $3CaOAl_2O_3$, whilst at a still higher temperature these appear to dissociate and form $3CaOAl_2O_3$ and $3CaOSiO_2$, the latter finally dissociating into $2CaOSiO_2$ and free CaO. Cobb's experiments seem to indicate that the simple calcium silicates and aluminates are formed at lower temperatures and ternary compounds at higher ones.

E. Selch [1] found that at Cone 04*a* two molecules of lime are required to decompose one molecule of clay, whilst at Cone 9 only one molecule is required.

[1] *Sprechsaal*, **173** (1916); **55**, 1, 2 (1922).

The **potash-alumina-silica system**, according to B. A. Rice,[1] has three eutectics, namely :—

TABLE CXXII.—*Eutectics of Potash-Alumina-Silica System*

	Percentage Composition.			Molecular Composition.			Approximate Temperature of Deformation, ° C.
	Potash.	Alumina.	Silica.	K_2O.	Al_2O_3.	SiO_2.	
1.	55·0	..	45·0	1·0	..	1·291	780
2.	17·5	..	82·5	1·0	..	7·430	880
3.	17·4	5·2	77·4	1·0	0·276	6·978	870

Two of these eutectics are devoid of alumina, but are not simple silicates ; the ternary eutectic contains much more silica and much less alumina than potash felspar. The system had two areas of low fusibility, one with high alkali, low silica, and low alumina, and the other with high silica, low alkali, and low alumina.

The **soda-alumina-silica system** (fig. 44), according to Wallace,[2] includes the following :—

I. *Compounds* :

(*a*) triple oxides—soda leucite ($NaAlSi_2O_6$), nepheline ($NaAlSiO_4$). In Nature, albite ($Na_2OAl_2O_36SiO_2$) also occurs, but its position with reference to this system is not known.

(*b*) Double oxides—sillimanite, andalusite, and kyanite (Al_2SiO_5).

(*c*) Single oxides—corundum (Al_2O_3), quartz, and tridymite (SiO_2).

II. *Mixed Crystals* :

(i) Sillimanite with corundum.
(ii) Sillimanite with silica.
(iii) Corundum with soda.
(iv) Nepheline with corundum.
(v) Nepheline with silica and sodium silicate.
(vi) Sodium silicate with silica.

B. A. Rice [1] has found that there are three eutectics as follows :—

TABLE CXXIII.—*Eutectics of Soda-Alumina-Silica System.*

	Percentage Composition.			Molecular Composition.			Approximate Temperature of Deformation, ° C.
	Soda.	Alumina.	Silica.	Na_2O.	Al_2O_3.	SiO_2.	
1.	51·5	..	48·5	1·0	..	0·972	830
2.	18·4	..	81·6	1·0	..	4·579	860
3.	17·5	5·4	77·1	1·0	0·185	4·550	800

[1] *J. Amer. Cer. Soc.*, **6**, 525 (1923). [2] *Loc. cit.*, p. 476.

As in the corresponding potash system, two of the eutectics are devoid of alumina; the ternary eutectic has less alumina than any natural sodium alumino-silicate. The system contains two areas of low fusibility, one with high alkali, low silica, and low alumina, and the other with high silica, low alkali, and low alumina.

Soda and its simpler compounds are among the most powerful fluxes which occur in ceramic materials and are the cause of much corrosion of refractory materials and the formation of fused silicates, aluminates, and alumino-silicates. Many of the members of the soda-alumina-silica system are readily fusible and in the molten state form very mobile liquids which readily penetrate the pores of firebricks, etc. Some of them absorb silica, readily forming mixed solutions, and these, when molten, are the cause of the loss of shape which usually occurs when clays, etc., are heated in the presence of soda, either as an impurity or otherwise (Chapter XIII.). In some cases, the sodium may be derived from sources which are easily overlooked, such as the small proportion of salt which occurs in some coals. This salt volatilises, decrepitates, and decomposes in the presence of moisture, and, at a temperature of about 800° C., combines with the clay or other siliceous material, forming compounds which belong to this ternary system (see *Salt glaze*, p. 391).

In the **barium-oxide-alumina-silica system** the most fusible mixture, according to A. S. Watts,[1] is intermediate in composition between (*a*) 35 per cent. barium oxide, 10 per cent. alumina, and 55 per cent. of silica, and (*b*) 40 per cent. of barium oxide, 10 per cent. of alumina, and 50 per cent. of silica, both of which mixtures show signs of fusion at Cone 6 (1200° C.), though are not completely molten at that temperature.

The **magnesia-alumina-silica system** (fig. 45) may, according to G. A. Rankin and H. E. Merwin,[2] contain all the compounds found in the corresponding binary systems, namely, forsterite ($2MgOSiO_2$), clinœnstatite ($MgOSiO_2$), sillimanite ($Al_2O_3SiO_2$), and spinel ($MgOAl_2O_3$), besides simple oxides and also a ternary compound $2MgO2Al_2O_35SiO_2$, which occurs in two forms with a variable inversion-point ranging from 925°–1150° C.

N. L. Bowen[3] found several eutectics between clay and magnesia at different temperatures, one between periclase and forsterite melts at 1850° C. (40° C. below that of forsterite), and one between clinœnstatite and silica melts at 1543° C. He did not find any eutectic between forsterite and clinœnstatite.

According to A. S. Watts,[4] the most fusible mixture of this system contains 20 per cent. each of magnesia and alumina and 60 per cent. of silica, corresponding to $MgO\ 0{\cdot}392Al_2O_3\ 2SiO_2$, which fuses at Cone 12 (1350° C.), but, according to Rieke, the eutectic of the magnesia and china clay system (m.-pt. 1300° C.) consists of ten parts of clay to nine parts of magnesia, corresponding to the formula $5MgOAl_2O_32SiO_2$.

[1] *Trans. Amer. Cer. Soc.*, **19**, 457 (1917).
[2] *Amer. J. Sci.*, **45**, 301 (1918).
[3] *Ibid.*, (4), **38**, 307 (1914).
[4] *Trans. Amer. Cer. Soc.*, **19**, 453 (1917).

The **zinc-alumina-silica system**, which includes the substance produced by the action of zinc oxide upon clay, gives rise to various compounds, the chief of which are :

(*a*) Zinc orthosilicate (willemite) ($2ZnOSiO_2$).
(*b*) Zinc metasilicate ($ZnOSiO_2$).
(*c*) Zinc spinel ($ZnAl_2O_4$ gahnite).

When iron oxide is present as an impurity, an isomorphous mixture of zinc and ferrous silicates may be formed. Stelzner [1] states that a mixture corresponding to $4Fe_2SiO_4Zn_2SiO_2$ forms homogeneous orthorhombic crystals, whilst some natural fayalites (p. 416) contain as much as 5 per cent. of zinc oxide, and stirlingite contains 10 per cent. Zinc and ferrous silicates are, therefore, isomorphous or at least partially so.

Quarternary and other Systems

Quarternary systems containing silica are often very complex on account of the number of compounds, solid solutions, and eutectics which are theoretically possible. Such systems may not only have the complexities of the ternary systems (including those arising from the dual behaviour of alumina), but the presence of an additional base or metallic oxide greatly increases the number of possible substances. There are further complications due to the different behaviour of systems obtained by heating four separate oxides and those resulting from the fusion of two binary systems or a ternary system with a single oxide. Thus, according to Schurecht,[2] excluding carbon dioxide, eutectics, and solid solutions, at least sixteen definite compounds may be formed during the burning of crude dolomite. They are produced by the reaction of five substances : lime, magnesia, ferric oxide, alumina, and silica.

$CaSiO_3$	$3CaOAl_2O_3$	$CaOFe_2O_3$
$3CaO2SiO_2$	$5CaO3Al_2O_3$	$Al_2O_3SiO_2$
$2CaOSiO_2$	$CaOAl_2O_3$	$CaOAl_2O_32SiO_2$
$3CaOSiO_2$	$3CaO5Al_2O_3$	$2CaOAl_2O_3SiO_2$
$CaOMgOSiO_2$	$2CaOFe_2O_3$	$3CaOAl_2O_3SiO_2$.

Similarly, felspar (which forms part of a ternary system) produces, according to Bleininger,[3] eutectics with iron oxide and lime, respectively, in the proportions shown below :—

91 parts of felspar to 9 parts of iron oxide (m.-pt. 1100° C.).
97 parts of felspar to 3 parts of whiting (m.-pt. 1100° C.).

Very complex eutectics are sometimes formed. Thus, according to Ferguson and Buddington,[4] akermanite ($2CaOMgO2SiO_2$) and gehlenite ($2CaOAl_2O_3SiO_2$) form an

[1] *Neues Jahrb. Min.*, **1**, 170 (1882).
[2] *J. Amer. Cer. Soc.*, **4**, 128 (1921).
[3] *Trans. Amer. Cer. Soc.*, **10**, 259–263 (1908).
[4] *Amer. J. Sci.*, (4) **50**, 131–140 (1920).

eutectic containing 74 per cent. of akermanite and 26 per cent. of gehlenite. The crystals of this eutectic have the same character as the minerals from which they are obtained, and mixtures of akermanite and gehlenite in various proportions form an isomorphous series.

Orthoclase and albite felspars form a non-continuous series of solid solutions or mixed crystals, but albite and anorthite dissolve in each other in all proportions. Felspar and mica dissolve clay, but the products do not show any eutectic composition. Felspar and flint show a pronounced eutectic.

Felspar dissolves clay more readily than flint. According to Mellor,[1] at the temperature of a potter's oven, felspar will dissolve about 20 per cent. of china clay, but only about 15 per cent. of flint. On the other hand, R. C. Purdy [2] and, independently, Zoellner consider that flint is more soluble in felspar than clay. Zoellner found that at the temperature of a porcelain kiln (Cone 15) felspar will dissolve 14 per cent. of clay substance and 60–70 per cent. of quartz. Bunzli found that felspar could dissolve 70 per cent. of its weight of flint in a crystalline form, and as much as 100 per cent. of amorphous flint, but the conditions under which these great solubilities were obtained were not precisely stated.

Muscovite and alumina, according to Rieke, form an eutectic consisting of 90 per cent. of mica and 10 per cent. of alumina, which fuses at Cone 12 (1375° C.).

The number of mathematically possible combinations of any four substances taken in groups of two, three, or four at a time can be determined by regarding them as permutations, in which case the numbers are :

6 binary combinations,
4 ternary combinations,
1 quaternary combination,

but in ceramic materials the number of original substances is not limited to four ; a much larger number may be present as (if those present in very small proportions are included) there may be ten or more metallic oxides in addition to alumina, silica, and various " acid oxides."

With such complex mixtures and compounds capable of existence, it is almost impossible to predict exactly what will be formed in any given case, because the presence of a small amount of impurity may greatly increase the number of substances which may be produced. In an attempt to simplify the subject and enable general comparisons to be made, the method of calculation by *norms* (p. 315) has been applied with considerable success both to igneous rocks and to ceramic materials. The weakness of " norm " calculations lies in the uncertainty as to what compounds are likely to be present, especially in view of the multiplicity of compounds and solid solutions which are possibly contained in a material, and by the fact that when more than one of these or any other fluxing agent is present, their combined action is greater than that of an equal weight of any flux when taken separately.

[1] *Trans. Eng. Cer. Soc.*, **7**, 97 (1907–08).
[2] *Trans. Amer. Cer. Soc.*, **13**, 479 (1911).

Great caution is necessary in applying the ideas of chemical equilibrium, the phase rule and solid solutions to ceramic materials. In few, if any, such materials is a state of true equilibrium ever reached, and comparatively small changes may, under such conditions, have remarkable results. In most clay products, fusion is far from complete, so that the data relating to various "systems" are only partially applicable and may prove misleading. The effect of Wenzel's law that "reactions proceed in proportion to the contact-area of the reacting surfaces" must never be overlooked, and, consequently, the sizes of the various particles is of great importance. Consequently, the data given in the foregoing pages must be used with discretion and skill, or the consequences may be serious.

FUSION

The term "fusion" in connection with ceramic and allied materials is applied to any treatment (usually the application of heat) which results in the conversion of a substance from the solid to the liquid or molten state. As explained on p. 438, where small quantities of a substance are heated to the melting-point, the change from the solid to the liquid state occurs rapidly and without any rise in the temperature of the substance until the substance is completely liquefied and fusion is complete. When large quantities are heated, especially if the substance has a low thermal conductivity, or is not quite pure, signs of fusion may appear at a temperature much below that at which liquefaction is complete. If the original substance is porous, a stage may be reached in which the pores are filled with liquid produced by partial fusion of the materials; this liquid solidifies on cooling, and the cold mass is then said to be *vitrified*. If the heating is continued at a suitable temperature, the whole of the material will become liquid and the mass is then said to be "completely fused." [1]

The "melting-, fusing-, or solidifying-point" of a substance is defined as the temperature at which its solid and liquid phases are in equilibrium at atmospheric pressure, but the temperature at which a silicate melts and that at which it solidifies may differ considerably owing to the effects of supersaturation and supercooling which are often extremely difficult to avoid.

The nature of the physico-chemical reactions which take place during the fusion of one or more ceramic materials can best be learned from a careful study of the appropriate equilibrium diagrams (pp. 454–484), but the fact should be borne in mind that there is very little evidence as to the nature of the substances which are produced in the earlier stages of fusion, as most of the information which has been obtained relates to substances which have been either partially or completely heated and afterwards cooled prior to investigation. It is certain, however, that the change of state from solid to liquid or *vice versa* of any substance is limited by certain critical

[1] The term *fused* is also applied to substances which have undergone fusion even though they have afterwards been allowed to cool and have become solid. "Fused quartz," for example, is a solid, glass-like material which owes its name to the fact that it is produced by fusing quartz. Unless care is taken, confusion may arise from this dual use of the word "fused."

conditions which determine which substances may exist and in what forms. These limiting factors which separate the solid from the liquid state [1] are :—

(*a*) The *critical temperature*, above which the substance cannot exist as a solid.
(*b*) The *critical pressure* at which the solid phase is formed when the substance is at the critical temperature.
(*c*) The *critical density*, which is the density of the solid substance when at the critical temperature and pressure. At the critical temperature the density of a solid is the same as that of its saturated vapour.
(*d*) The *critical volume*, which is the volume of 1 gramme of the substance when at the critical temperature and pressure.

The combined effect of these various factors is often complicated, especially as the presence of even a small proportion of impurity alters the melting-point of a substance. A change of pressure (unless it is very great) does not greatly affect the melting-point.

When a clay or other ceramic material is heated very slowly, as under industrial conditions, the general order in which the changes leading to fusion occur is as follows : the smaller particles on the exterior of the mass tend to fuse first ; they are followed by gradually increasing particles on the exterior. Later the particles nearer the interior behave in a similar manner. If the mass contains several substances (*e.g.* if it is impure) they will melt in approximately the order of the fusibility, though reactions which take place between some of them may alter this order considerably. This is particularly the case where a ceramic " body " or glaze contains a considerable proportion of fluxes, added so as to form a vitrifiable or glassy material which may form either a small, medium, or large proportion of the final product according as the latter is intended to be porous, vitrified, or completely fused. In any given mixture—provided the proportion of bases to silica is sufficient—the amount of fused material produced will depend on the temperature and duration of the heating ; the higher the temperature or the longer the heating the greater will be the amount of fusion.

In most ceramic materials, little glass is produced below a temperature of 1000° C. unless a considerable proportion of soda is present. The glassy matter usually begins to develop at about 1140° C., and increases fairly rapidly up to about 1250° C., the felspar fusing readily about this temperature. The partial fusion continues rapidly up to about 1300° C., the fused material dissolving the smaller particles and thus increasing the volume of the fused product. After this, the fusion proceeds more slowly, with a steady rise in temperature, because the alumino-silicates are more viscous and flow less readily than the simple silicates and so require a longer time to effect an equal amount of corrosion.

Quartz particles begin to show signs of fusion or solution on their edges at about 1280° C., the action becoming more rapid with an increase of temperature, and (on

[1] In some cases, such as iodine, ammonium chloride, etc., solids may be converted directly from the solid into the gaseous state without previous liquefaction, in which case the critical point will be between the solid and gaseous states. Such substances are said to *sublime*.

prolonged heating) at 1320° C. most of the quartz is dissolved, the remaining particles being rounded as a result of their edges having been dissolved. If sufficient fluxes are present, as in a glaze, complete solution of the quartz and fusion of the whole material may occur at as low a temperature as 900° C.

Felspar particles remain unchanged until a temperature of about 1100° C. is reached, but above this temperature they begin to fuse, and on prolonged heating at 1180° C. they are usually fused and completely mixed with the glassy product, notwithstanding the fact that the fusion-point of felspar, when heated alone, is above this temperature, pure orthoclase melting at about 1200° C. and commercial felspar in comparatively large pieces melting at about 1280° C.

In a mixture of hard felspar, clay, and flint, such as is used in the manufacture of porcelain, the felspar begins to exercise a noticeable solvent action at about 1280° C., attacking first the clay particles and then the flint. At about 1300° C., sillimanite begins to crystallise out, and at about 1380° C. the felspar is completely fused. According to A. S. Watts,[1] the same amount of fusion or solution occurs with soda felspar at 1300° C. as occurs at 1340° C. with potash felspar.

It is impossible to devise simple formulæ which will indicate the rate of fusion in terms of time and temperature, because it also depends very largely on the size of the grains of material, on the surface exposed to chemical action, and on the viscosity of fused products; the last-named depends on the nature of these products, some substances producing much more viscous fluids than others. Thus, magnesia produces a very viscous slag or glass, and, consequently, the range of temperature through which fusion occurs (sometimes termed the *vitrification range*) is much longer where magnesia is the chief flux present than when lime is present in considerable proportion. Thus, articles containing magnesia as a flux are less likely to soften and lose their shape than those in which lime is used.

The rate of fusion also depends on the solubility of the less fusible materials in the liquid portion. This, in turn, depends partly on their mutual reactability, a fusible mobile silicate rich in bases having a much greater solvent action than one—such as felspar—of a more neutral character. The action of felspar is very slow, so that it does not cause the ware to lose shape very quickly as is the case when calcium silicate is the chief constituent of the fused portion of the material.

The constitution of fused masses is by no means fully understood and there is much difference of opinion regarding the chemical constitution of completely fused salts. Some investigators maintain that such masses are composed of definitely molecular compounds, whilst others regard them as dissociated into free oxides.

According to Sosman,[2] the regularity of the curve of the relation between the specific volume and the molecular composition of molten substances does not favour the existence of compounds in the molten mass, and the idea now generally favoured regards completely fused materials as similar to some extent to dilute solutions which are, to a varying extent, dissociated into ions. This view is supported by the experiments of Barus and Iddings, from which it appears that silicates are more strongly dissociated than basic materials, which would account for the fact, pointed

[1] *Trans. Amer. Cer. Soc.*, **11**, 185 (1909). [2] *Loc. cit.*, p. 469.

out by Doelter, that basic minerals separate more easily from slags than do silicates. On the other hand, pure silica, when fused, is not appreciably dissociated. If it is correct that some fused masses are in a dissociated condition, the effect of a common ion should be similar to its effect in aqueous solutions. This " common ion theory " has been used to explain the behaviour of eutectics (p. 461).

It is very probable that some fused substances which produce mixed crystals on cooling do not contain such compounds when in the molten state. It is much more likely that the separate components of the mixed crystals existed independently in the molten mass. For instance, fayalite may exist as forsterite and iron olivine, whilst labradorite may be in the form of separate molecules of albite and anorthite.

The Solidification of Molten Masses.—When a molten mass cools it eventually becomes solid, but the physical and chemical nature of the solid produced may vary greatly, according to the nature of the materials present and the rate of cooling.

The passage from the liquid to the solid state consists essentially in the limitation of movement of the molecules. This freedom is greatest at a high temperature, and if the temperature is reduced sufficiently the molecules must be arrested and the substance then enters the solid state. If the arrest is instantaneous, the molecules may be unable to arrange themselves according to their polarity, and the solid mass then consists of a heterogeneous arrangement of molecules. Thus, the fully cooled solid may consist of : (*a*) a homogeneous glass, (*b*) a wholly crystalline mass, or (*c*) a heterogeneous mixture of both crystals and glass. On cooling sufficiently, a homogeneous liquid acquires, in general, the property of crystallising, but this requires both time and freedom of movement.[1] If either or both of these factors are lacking—as when the liquid is cooled too quickly and too intensely—it may solidify without crystallising and is then said to be " undercooled." Such undercooled liquids may form relatively stable solids, which are then termed *amorphous* (in opposition to crystalline) solids.

An amorphous substance has the external appearance of a solid with great viscosity and rigidity, but it differs from a crystal in its complete isotropy and in the absence of a definite melting-point ; on heating it passes gradually into a liquid state and its properties change steadily with a rise in temperature. Quartz-glass, glasses (silicates), and many metallic oxides are typical examples of amorphous substances.

Substances in the vitreous state are in a state of elastic strain, but their elasticity is restored by heating to a temperature within the range of crystallisation.

In the vitreous state, energy is stored in the molecules as in a collection of coiled springs ; it becomes kinetic when the molecules are set free by the action of heat upon the aggregate. The energy then supplies heat to the system which would, otherwise, have to be drawn from an outside source.

The stability of a vitreous solid depends on the temperature. If the solid is heated it may liquefy, or the heat may impart just sufficient freedom to the

[1] The degree of freedom necessary for crystallisation may occur at a temperature much below that of fusion. Alternatively, the vitreous state may be produced by a gradual increase in the viscosity of the liquid phase.

constituent molecules for their polarity to come into play so that the mass crystallises. The stability of a crystalline solid persists from the transition temperature to the fusion-point.

Liebisch [1] has shown that the regular heating of an amorphous mass usually causes it to crystallise, *e.g.* gadolinite, devitrifiable glasses, etc., but, in some cases, the presence of a crystal of the same or an amorphous substance appears to be necessary for the complete crystallisation of a liquid.

The physical conditions which influence crystallisation include the following :—

(*a*) The *temperature attained* during heating and the duration of the heating. Thus, silica glass tends to crystallise if it is maintained at a temperature between 1200° and 1600° C. for a long period, the amount of devitrification depending on the duration of the heating. R. Sosman has found devitrification to take place when silica glass is heated between 200° and 275° C. for a long time. This is known as the α-β transition range.

A. A. Klein [2] found that the microstructure of porcelains depends more on the attainment of a high temperature than on prolonged heating at a lower temperature. Thus, porcelains heated to Cones 13–14 and maintained at that temperature for 12–108 hours consisted chiefly of amorphous sillimanite with a few crystals of sillimanite, but a porcelain heated to Cone 15 and maintained at that temperature for only one hour consisted chiefly of sillimanite crystals with practically no amorphous sillimanite. It is unusual, however, to find so great an increase in the velocity of crystallisation to occur with so small an increase of temperature.

(*b*) The *viscosity of the molten fluid*, as excessive viscosity hinders the crystallisation of fused glasses, etc., by hindering the motion of the particles.

Substances like silicates and borates with a high velocity and a high crystallising temperature are easily cooled at a rapid rate through the whole range of crystallisation and thus, most naturally, pass into the vitreous state on cooling.

Tamman [3] has shown that the viscosity of molten substances increases during the cooling, the corresponding graph being in the form of a parabolic curve. Doelter suggests that the feeble mobility of the ions in a fluid having a high viscosity when at the freezing-point hinders the production of ionic equilibrium and, consequently, hinders crystallisation, the substance remaining dissociated. This agrees with Roozeboom's theory that in substances with a sharp melting-point the ionisation equilibrium is readily established. The viscosity also affects the size of the crystals, the most viscous fluids producing the finest-grained masses. Conversely, to produce large crystals a very mobile fluid must be employed.

(*c*) The *rate of cooling* influences both the amount of crystallisation and the composition of the crystals. Slow cooling favours crystallisation, whilst rapid cooling retards it. If the cooling is very rapid no crystals may be formed at all, the whole mass then consisting of a homogeneous glass. Hence, where crystallisation is to be avoided, rapid cooling through the crystallising range (p. 489) is essential, but where

[1] *Berl. Akad. Ber.*, **1**, 350 (1910).
[2] *J. Amer. Cer. Soc.*, **3**, 978 (1920).
[3] *Sprechsaal*, **35** (1904).

a crystalline mass is desired, slow cooling is necessary. Some glasses and glazes have a great tendency to crystallise if allowed to cool very slowly between 860° and 790° C., but the precise range varies according to the constituents of the glass or glaze.

When a fused mass, on cooling, forms mixed crystals, the composition of the crystals varies according to the rate of cooling. Thus, if the cooling is completed before the system has reached a state of equilibrium, the composition of the crystals will be different from what would be the case if the cooling had been much slower. These variations in composition are due to the fact that the solidification of mixed crystals takes place through a range of temperatures and not at a fixed point, the composition of the solid and liquid portions changing progressively, provided the rate of heating or cooling is sufficiently slow to permit it to do so. It is probable that the dual materials present in mixed crystals are combined during the cooling and that in the fused mass they exist as separate substances.

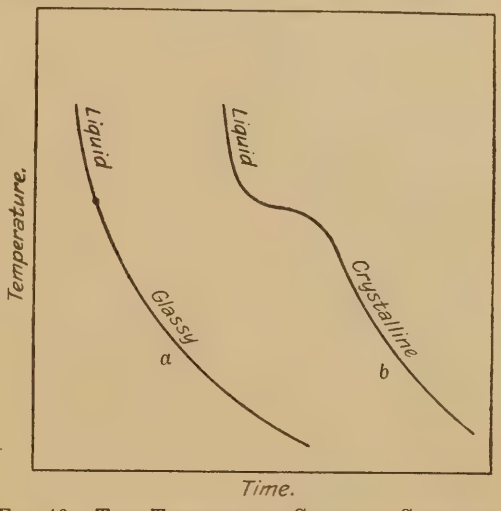


Fig. 46.—Time-Temperature Curves of Crystals and Glass.

A study of the time-temperature curves of a fused substance during slow cooling is very interesting in connection with the phenomena of crystallisation. Thus, if a thermo-couple is inserted in the fused mass and the temperature of the latter is noted at regular intervals of time, it will be found that if the cold product is a homogeneous glass, there will be no critical point, the cooling curve being perfectly regular (fig. 46 *a*). At the temperature when crystallisation occurs, however, there is a definite kink in the cooling curve, as shown in fig. 46 *b*. The "flat" in the second curve indicates that the temperature ceases to fall until all the matter which can crystallise at that temperature has done so, after which the fall in temperature continues. Precisely the same curve is produced when the crystalline substance is melted (see *Time-Temperature Curves*, p. 464). When several substances, capable of crystallising at different temperatures, are present, a series of "steps" is produced in the cooling curve.

(*d*) The *number of centres of crystallisation* formed in a definite area per second. According to Tamman, the presence of a *mineraliser* increases the crystallisation capacity, but does not affect the crystallisation velocity. In the complete absence of "dust" or of any substance—preferably a minute crystal of the substance in the fused material or of a compound isomorphous with it—crystallisation may be delayed indefinitely, but will occur rapidly in the presence of one of these "mineralisers" or "nuclei."

Other Chemical Reactions occurring at High Temperatures

Among other important chemical reactions which occur between or in connection with ceramic materials at high temperatures are those best grouped under the four captions: (*a*) decomposition, (*b*) oxidation, (*c*) reduction, and (*d*) corrosion. Some of these reactions have already been mentioned, but they are so important in connection with the group-terms used to distinguish them, that a brief mention of these is desirable.

Decomposition

Decomposition is the splitting up of compounds into simpler substances (p. 436). It may be of two kinds:

(*a*) *Dissociation*, in which the substance is divided into two or more substances, no others taking part in the reaction.

(*b*) *Decomposition by reaction* with other substances (see *Double Decomposition*, p. 436).

A typical example of dissociation is observed when clay is heated and the water which is chemically combined with it is evolved as a result of the decomposition of the material. It is probable that the decomposition begins at a comparatively low temperature, probably 200°–250° C., but the water does not escape in large proportions until a temperature of about 450° C. is reached. For this reason, it is often considered that the decomposition of clay with evolution of water commences at about 450° C. Bauxites are also decomposed at 600° C. with the loss of their combined water, but as the reaction is very slow, except at high temperatures, the calcination of bauxite is generally carried out at temperatures above 1200° C.

Various carbonates, such as calcite, magnesite, and dolomite, are decomposed by heating (burning) them in kilns so as to produce the corresponding oxides, which are highly refractory. The action in each case is typically represented by the following equations:—

$$CaCO_3(+\text{heat}) \rightleftharpoons CaO + CO_2$$
$$CaMg(CO_3)_2(+\text{heat}) \rightleftharpoons CaO + MgO + 2CO_2.$$

The evolution of carbon dioxide from calcium carbonate commences between 600° C. and 725° C. and continues up to 850°–900° C.

When carbon dioxide is driven off from a carbonate the residual oxide rapidly combines with any other suitable material if present. Alternatively, the presence of such a material (*e.g.* an acid, silica, or clay) may cause the carbon dioxide to be evolved at a lower temperature than when the carbonate is heated alone. This is due to the mutual affinity of the oxide (lime) and the acid being greater than that of the oxide (lime) and carbon dioxide.

Magnesium carbonate is decomposed at 800°–900° C. with the evolution of carbon dioxide, the residue being caustic magnesium oxide or magnesia. At higher temperatures, the magnesia is crystallised and forms periclase.

Dolomite is decomposed in two stages when heated, the carbon dioxide in the

magnesium carbonate being evolved first and that in the calcium carbonate at a higher temperature.

Some impurities may be decomposed and volatilised during the heating; thus, sulphates are decomposed, forming sulphur dioxide or sulphur trioxide; carbonates present may be decomposed as previously described; organic matter may be oxidised, forming water and carbon dioxide; various iron compounds may either be dissociated or they may react with clay, etc., and so be decomposed.

The decomposition of sulphates takes place at a higher temperature than that of carbonates, usually about 800°–1000° C., evolving sulphur trioxide in an oxidising atmosphere. If an excess of silica is present, the dissociation is replaced by a double decomposition which occurs at a slightly lower temperature and silicates are formed.

Unintentional, and sometimes undesirable, dissociations and decompositions sometimes take place when clays and other ceramic materials are heated to too high a temperature in use. Thus, carborundum when heated to about 1250° C., decomposes slowly, the silica being volatilised and the carbon burning to carbon dioxide and escaping. This decomposition takes place without any general fusion of the mass. If the carborundum is not very pure or the atmosphere in which it is heated is dusty (as is usually the case with flue- or kiln-gases), a siliceous glaze sometimes forms on the surface of the carborundum and prevents, or at any rate hinders, the decomposition of the mass under ordinary conditions of use. Other carbides and carboxides are similarly decomposed when heated to too high a temperature, but siloxicon is more easily oxidised than carborundum, though if heated in a neutral or reducing atmosphere it is not affected until it reaches 1840° C., when it commences to decompose, forming carborundum, free silica, and carbon monoxide.

The interaction of furnace linings, walls of retorts, crucibles, and other refractory articles with their contents is typical of a series of undesirable decompositions which are of great technical importance. They are described under the caption *Corrosion* on pp. 494–503.

Oxidation

Oxidation plays an important part in the various reactions involved in the production of ceramic articles. The chief technical objects of oxidation are:

(*a*) The conversion of impurities by weathering or during the burning process (*i.e.* carbon, sulphur, etc.) into a form which can easily be removed, as by their conversion into gases or soluble substances.

(*b*) The oxidation of iron compounds either to render them more refractory or for the production of a desirable colour, as in the manufacture of red bricks, terra-cotta, etc.

The removal of **carbonaceous matter** is most readily effected by oxidation, *i.e.* by heating it in a suitable atmosphere in which it combines with oxygen, forming carbon dioxide and water, both of which escape as gases. The decomposition occurs most rapidly between 800° and 900° C., though it commences at a much lower temperature. In many cases, it is a matter of great technical importance that all the

carbonaceous matter should be oxidised in the early stages of the burning process, as otherwise it will be impossible to oxidise the iron compounds. If the ceramic material is heated too rapidly superficial fusion may occur, sealing the pores, preventing all access of air to the interior, and so making it impossible to burn off all the carbon (p. 423). If, on the contrary, the temperature rises slowly and is not allowed to exceed about 900° C., the removal of the carbonaceous matter by oxidation is comparatively simple.

Sulphides are decomposed when heated, if the atmosphere is oxidising, sulphates or sulphur dioxide and a sulphate being formed. Pyrites (FeS_2) loses 60–75 per cent. of its sulphur at a temperature below 800° C. and the remainder above this temperature. The latter is removed very slowly, the evolution decreasing in rapidity as the temperature rises; usually some combination occurs and a corresponding proportion of sulphur is never expelled.

Ferrous compounds are oxidised to the corresponding ferric compounds or to red ferric oxide when they are heated in a current of air. A temperature of 900° C. is usually required for rapid oxidation, but if the temperature is very high the red ferric oxide (Fe_2O_3) may be decomposed and magnetic iron oxide (Fe_3O_4) produced. A rather peculiar case of oxidation of metallic iron sometimes occurs in furnaces, because in the presence of free iron or metals of the iron group, carbon dioxide dissociates into carbon, carbon monoxide, and oxygen, the carbon being deposited on the bricks and some of the free iron is oxidised to FeO. The action appears to occur at different temperatures, according to the pressure, as shown in Table CXXIV (due to Harvard).

TABLE CXXIV.—*Oxidation of Ferrous Oxide*

Pressure, mm.	Temperature, ° C.	Pressure, mm.	Temperature, ° C.
15	500	305	700
35	550	535	750
70	600	800	800
145	650	..	..

In most commercial furnaces the action does not take place below 690° C.

It may be observed that the oxidation of the impurities in clays does not usually take place until a temperature of 800° C. or above is reached, though peaty matter and limonite are decomposed much below this temperature, and Purdy and Moore [1] have pointed out that the oxidation of the impurities in some clays occurs before the clay is completely dehydrated.

REDUCTION

Reduction plays both a useful and a harmful part in the chemical reactions connected with ceramic processes. The chief reducing agents used in connection

[1] *Trans. Amer. Cer. Soc.*, 9, 204 (1907).

with ceramic materials are carbon monoxide and hydrogen (generally produced by burning coal with an insufficient amount of air), but finely divided carbon and several metals have a powerful reducing action when at a sufficiently high temperature. The presence of sulphur dioxide in the kiln-gases, as occurs when a sulphurous coal is used, has a reducing effect upon any iron oxide present and may produce ferrous compounds. Sulphur trioxide, if present in the kiln-gases, may attack the bases present in the clay and form sulphates. If an oxidising atmosphere is maintained these sulphates will persist and may produce a scum on the goods, but if reducing conditions arise they will be decomposed again.

Silica is reduced by carbon at temperatures above 1200° C., forming the element silicon and carbon monoxide. The reaction is more rapid in the presence of iron and some other metallic substances. In some cases, silicon carbide may be produced (*below*). Zirconia, when heated to very high temperatures, tends to be reduced by its combination with carbon, forming zirconium carbide.

As an instance of a *desirable* reducing action may be mentioned the production of a considerable amount of fluxing material from the iron compounds present, by the formation of fusible silicates as in the manufacture of blue bricks, in order to produce a vitrified mass of requisite strength and to produce the blue colour which is characteristic of ferrous silicates. The slightly bluish sheen of porcelain is due to the same cause. Some colours used in glazes require to be fired in a reducing atmosphere in order to produce the desired effect.

Reduction processes are sometimes used in the manufacture of refractory materials, such as silicon carbide, by the reduction of silica :—

$$SiO_2+3C=SiC+2CO.$$

The reaction begins, according to Lampen, and also to Tucker, Gillet, and Saunders, at a temperature of about 1820°–1920° C. ; other carbides and carboxides are prepared in a similar manner.

A reducing action may be *harmful* when it is produced accidentally, as it may result in the decomposition of a useful material and the production of undesirable fusible compounds. Thus, if fully oxidised iron compounds, such as ferric oxide, are reduced to the ferrous state, in contact with clay or silica, they immediately lower the refractoriness of the bodies in which they occur, because ferrous silicate is readily fusible and may, therefore, cause much trouble and loss. Carbon has a stronger affinity for oxygen than iron, and, consequently, no oxidation of the iron compounds can occur in the presence of carbonaceous matter. It is, therefore, necessary to use a highly oxidising atmosphere in the earlier stages of firing clays, etc., containing carbonaceous matter, in order to oxidise and remove the carbon. At a later stage, when all the carbonaceous matter has been burned away, some or all of the iron compounds may be reduced to the ferrous state without damaging the ware, but great care is needed in the control of the furnace or kiln, as in a reducing atmosphere at high temperatures the ferrous compounds will attack the silica present and form slag-like masses of fusible iron silicate.

Carbon has a greater affinity for oxygen than sulphur; consequently, it may retard

the oxidation of the latter, and, conversely, sulphates may, if required, be converted into sulphides by heating them in an atmosphere containing carbon monoxide or hydrogen at temperatures above 700° C. Reduction therefore forms a useful means of preventing the formation of " scum " caused by soluble sulphates.

Corrosion

Corrosion is a term which is applied to the result of a large number of chemical reactions of an undesired character. These reactions are the same as the desirable ones, but they occur at an unsuitable time. Thus, the action of iron oxide on magnesia or of lime on silica may be useful for the production of a suitable bond, but when these substances attack refractory materials whilst the latter are in use their effect is undesirable and may be included under the term " corrosion." The factors which influence corrosion are described on pp. 437–449. In addition to these, the situation of the material is often very important as regards the action of corrosive substances. Thus, the action of a flux is greater if it is in contact with the cooler side of the material than if it is in contact with the hottest surface. Thus, if the corrosive substance is gradually cooled as it penetrates the material, its action will be correspondingly lessened, but if the temperature increases as the corrosive substance penetrates the action will be intensified.

In some cases, the continued action of a corroding agent may, in time, prevent or hinder further action taking place. Thus, when calcium compounds attack fireclay a calcium alumino-silicate is first formed which is high in calcium and has a low fusing-point. As more clay is dissolved, the material formed becomes richer in alumina and silica and at the same time more refractory, so that in time a protective coating is formed and further corrosion is prevented or at least proceeds very slowly. There are three chief groups of substances which have a corrosive action on ceramic materials :

(*a*) Free bases which combine directly with clay, silica, etc.

(*b*) Silica, clay, and other materials which react like acids with basic refractory materials such as magnesite, etc.

(*c*) Salts which, on heating, are decomposed, liberating a base and an acid, the base uniting with the fireclay, silica, or analogous refractory material and producing a fusible compound. To this class belong substances such as calcium sulphate, sodium chloride, etc. Thus, the soluble salts present in some coals used for making gas or coke cause much trouble by corroding the material of which the retort or coke oven is made. Sodium chloride is usually the most important of these salts, though others may also be present.

(*d*) Direct-acting salts which act like free bases, though to a less degree. Felspar, mica, Cornish stone, etc., are of this class.

The chief corrosive agents to which clay, silica, and analogous materials are likely to be subjected are molten metals, slags, such as those produced in open-hearth, reverberatory, converting, and cupelling furnaces, consisting chiefly of basic, subsilicates or sesquisilicates (such as the slags produced in assaying),

and metallic oxides.[1] The action of volatilised substances may also be serious in some cases.

Lime should not be brought into contact with clay or silica at high temperatures or partial fusion may take place. Whiting ($CaCO_3$) attacks fireclay bricks in the same manner as lime, and so does Portland cement; the last-named, according to Hirsch, forms a calcium alumino-silicate, corresponding to the formula $2{\cdot}5CaOAl_2O_3 3SiO_2$. The action is not so intense as that of lime or calcium carbonate.

Iron compounds form ferrous or ferric alumino-silicates, the former being more fusible and, therefore, more corrosive than the ferric compounds. Iron oxide corrodes fireclay bricks more severely than silica bricks. Sulphides are also very corrosive and rapidly penetrate clay products and silica. Iron sulphide combines with silica to form fayalite ($FeOSiO_2$) and sulphur dioxide which escapes as a gas. Any sulphur which may be present in the fuel used in furnaces may exert a corrosive action upon the brickwork at high temperatures, the sulphur being converted first into sulphur dioxide and then into sulphuric acid which attacks the clay.

The presence of steam often facilitates the corrosive action of other substances; thus, its presence is necessary for the decomposition of some of the soluble salts in coal, and, for this reason, the preliminary drying of a coal may reduce the amount of corrosion of any firebricks with which it may be heated.

Fireclay bricks which are high in alumina are usually less easily corroded by fluxes, etc., than those rich in silica, but the amount or rate of corrosion is not always proportional to the total amount of alumina present. The solution of alumina by a slag containing a metasilicate may increase the fluidity of the slag and, therefore, increase its solvent action on bricks. With silicates richer in flux than metasilicates, however, the solution of alumina decreases the viscosity and increases the refractoriness of the bricks.

Howe, Phelps, and Ferguson[2] have found that the resistance of some fireclay bricks to corrosion by slag is increased by a high alumina-content, but some coal ashes (clinker) and some metallurgical slags attack highly aluminous bricks more readily than highly siliceous bricks.

Table CXXV shows the refractoriness of various mixtures of slag and refractory material, obtained in the slag-test devised by R. M. Howe, S. M. Phelps, and R. F. Ferguson (p. 503), in which the lowering of the refractoriness of a powdered mixture of slag and refractory material is regarded as the index of the intensity of the reaction.

Metallic vapours sometimes cause the destruction of firebricks. Thus, when vapours of metallic zinc penetrate the bricks of the blast furnaces in which the ores are smelted, they are oxidised by the CO_2 present and are solidified in the pores. This may cause disintegration if the bricks are not very strong. A similar corrosion occurs when zinc is smelted in retorts.

J. W. Cobb considers that the penetration of vapours of sodium chloride into fireclay retorts may cause the formation of ferrous chloride which will, in turn, volatilise and act as a corrosive agent.

[1] Very few crucibles will withstand prolonged heating when containing a mixture of red lead and copper oxide.

[2] *J. Amer. Cer. Soc.*, **6**, 589 (1923).

TABLE CXXV.—*Refractoriness of Mixtures of Slags and Fireclay Bricks (The Results are expressed in Seger Cones)*

Type of Slag.	Percentage of Slag in Mixture.								
	0.	4.	8.	12.	16.	20.	30.	40.	50.
Acid open-hearth . .	32	32	32	30	28	26	13	11	8
Blast furnace . . .	32	30	29	20	17	13	13	12	9
Basic open-hearth . .	32	30	26	16	15	13	9	8	5
Heating furnace . .	32	31	30	26	19	18	10	9	8
Coal ash (clinker) . .	32	32	32	31	31	31	30	29	20

Flue-dust has a complex action upon firebricks producing a fusible mixture of various silicates and alumino-silicates, according to the composition of the dust. Mellor and Emery [1] determined the action of various corrosive flue-dusts upon clays and siliceous refractory materials with the following results :—

TABLE CXXVI.—*Corrosive Action of Various Flue-Dusts*

	Firebrick.	Silica Bricks.	Fine-grained Silica Brick.
Boiler flue-dust high in lime and ferric oxide	dP mC	..	..
Ferruginous boiler flue-dust .	sP sC	..	..
Ochreous dust from retort brick.	kP sC	dP gC	..
Basic slag	dP sC	dP mC	..
Ferruginous dust high in lime .	kP mC	dP mC	..
Bull dog	..	dP sC	..
Hæmatite (reducing flame) .	..	dP sC	sP sC
Tap cinder	dP mC	dP mC	dP sC
Lime	sP mC	sP mC	..
Lime and salt	sP mC	sP mC	..
Salt	dP sC	sP mC	..
Sodium sulphate . . .	sP sC	sP mC	..
Salt and felspar . . .	sP sC	sP mC	..
Soda lime-glass . . .	sP sC	sP mC	..

P=penetration. k=complete.
s=slight. m=medium.
d=deep. C=corrosion.
gC=great corrosion or slagging.

[1] *Trans. Amer. Cer. Soc.*, **18**, 230 (1918–19).

Mellor and Emery found that the oxides of copper, zinc, and iron in a finely divided condition have a very high penetrative power under reducing conditions at very low temperatures. Copper oxide will penetrate at 600° C. and iron at 1100° C. They found tap cinder to be the most corrosive dust amongst those they examined, though the dust from the slag chamber of a steel furnace is extremely corrosive.

Carbon monoxide and some hydrocarbon gases are decomposed by hot fireclay with the deposition of carbon in the pores. The latter may rupture the bricks. Blasberg has stated that the presence of less than ½ per cent. of carbon in a fireclay brick may cause its disintegration. When no disintegration occurs, a superficial deposition of carbon on refractory articles is sometimes an advantage, as it may protect them and prevent wear and corrosion.

Silica bricks have a more intense acid reaction at high temperatures than fireclay bricks, and consequently, if both kinds of bricks have a similar texture, the silica bricks are more rapidly attacked by basic fluxes such as slags, metallic ores, ashes, etc. As silica bricks are usually composed of coarser particles than clay bricks, the former are often the more resistant. Silica in silica bricks will combine with a greater proportion of lime than will an equal weight of fireclay. Silica bricks may increase slightly in refractoriness on prolonged heating, because the calcium silicates and alumino-silicates, formed at first, melt at a comparatively low temperature (about 1170° C.), but on prolonged heating they combine with more silica, and their fusion-point is raised proportionately. Silica bricks are less affected by iron oxide than are fireclay bricks when in an oxidising atmosphere, but they are rapidly attacked in a reducing atmosphere, because the ferrous oxide formed combines with the silica, forming fayalite ($2FeOSiO_2$). The action of slags upon silica bricks is greatest with those containing the highest proportion of alumina, so that silica bricks should be as low in alumina as possible.

According to the slag test devised by Howe, Phelps, and Ferguson (p. 503), silica bricks are highly resistant to acid open-hearth and heating-furnace slags which are chiefly composed of silica and iron oxide, but such bricks are not resistant to basic open-hearth and blast-furnace slags which are rich in lime. Table CXXVII shows results obtained by these investigators on the refractoriness of powdered mixtures of silica brick with different slags in various proportions.

TABLE CXXVII.—*Effect of Slags on Silica Bricks*
(*The Results are expressed in Seger Cones*)

Type of Slag.	Percentage of Slag.								
	0.	4.	8.	12.	16.	20.	30.	40.	50.
Acid open-hearth . .	31	31	31	31	31	29	28	28	28
Blast furnace . . .	31	31	31	30	30	27	17	6	3
Basic open-hearth . .	31	31	31	31	31	30	19	16	4
Heating furnace . .	31	30	29	28	28	28	28	27	26

Mortars and cements for silica bricks should be as low in alumina as possible, as highly aluminous cements react strongly with silica bricks.

Mellor and Emery [1] found the siliceous materials were affected by various fluxes in the manner shown in Table CXXVI. The bond of silica bricks is most easily corroded, so that a brick with interlocking grains and very little cement is most resistant to penetration and corrosion. In coarse-grained silica bricks, only the bond is attacked, but in fine-grained bricks both the bond and the silica grains are attacked.

Silica glass is attacked by various metallic oxides, such as copper oxide, lead oxide, and others, and also by many metals, including calcium, magnesium, aluminium, nickel, sodium, potassium, and cerium. These metals reduce silica at red heat to silicon. At 900°–1000° C., nickel-chrome wire exerts a strong corrosive action upon silica glass.

Silica glass is not so rapidly attacked by lime as finely ground silica, the action not being very great below 1400° C. Below this temperature, according to Hedvall, calcium monosilicate is formed, but above it a bisilicate is produced, the temperature of formation of the latter being 1390°–1420° C. with amorphous silica, and 1412°–1444° C. with crystalline silica.

Silica is volatilised in the presence of carbon on account of the latter reducing the silica to silicon, which is volatilised slowly at 1750° C. and more rapidly at higher temperatures. The volatilised element is reoxidised and re-forms silica. The British Thomson-Houston Co. found that the best conditions for volatilisation were obtained with a mixture consisting of 4 parts of silica, 2 parts of carbon, and 4 parts of fireclay, with or without 1 part of manganese oxide. In an oxidising atmosphere in the absence of carbon no volatilisation occurs.

Magnesia bricks are basic in character, yet they may be heated in contact with silica without much interaction occurring provided the bricks are sufficiently hard and dense and the temperature is not too high. For this reason, silica and magnesia bricks are sometimes used in the same furnace without any intermediate zone, though, as a matter of precaution, it is generally desirable to use an intermediate zone of neutral bricks.

Fireclay and magnesia bricks begin to interact seriously, according to Bischof, at about 1600° C., but M'Dowell and Howe found them to interact at about 1530° C. if lime is present to the extent of 3 per cent. Silica and magnesia bricks react strongly at 1610° C. Iron oxide alone has little effect upon magnesia, but in the presence of phosphorus much corrosion occurs.

When subjected to the slag-test devised by Howe, Phelps, and Ferguson (p. 503), magnesia bricks show a high resistance to basic open-hearth slag. Table CXXVIII shows results obtained by these investigators on the refractoriness of various powdered mixtures of slag and magnesia brick.

Carbon rapidly attacks magnesia bricks, and many carbides, including those of nickel and chromium, are even more destructive, the magnesia being practically reduced to magnesium. The action begins, according to Northrup, about 1450° C.

[1] *Loc. cit.*, p. 496.

and increases rapidly as the temperature rises ; M'Dowell and Howe found a loss of 27 per cent. at 2200° C. The action is intensified by the presence of lime. When magnesia bricks are heated in contact with carbon electrodes in an electric furnace they are greatly corroded ; in some cases, half the face of the bricks is removed.

TABLE CXXVIII.—*Effect of Slags on Magnesia Bricks*
(*The Results are expressed in Seger Cones*)

Type of Slag.	Percentage of Slag.				
	16.	20.	30.	40.	50.
Acid open-hearth .	36	33	32	31	27
Blast furnace . .	36	33	26	17	14

Magnesia bricks are also rapidly disintegrated by the action of steam, especially when such bricks are laid in a wet cement and then heated so as to dry them rapidly.

Bauxite bricks are generally regarded as basic, but they are probably almost neutral and do not behave as either truly acid or truly basic materials.

Bauxite bricks are not appreciably affected by basic slags, but they are much more strongly attacked by lime. If the surface of the bricks is dense, however, the rate of corrosion is very much reduced.

Table CXXIX, due to Howe, Phelps, and Ferguson (p. 503), shows the refractoriness of various powdered mixtures of slag and diaspore brick, and that bricks made of diaspore are very resistant to slags.

TABLE CXXIX.—*Effect of Slags on Diaspore Bricks*
(*The Results are expressed in Seger Cones*)

Type of Slag.	Percentage of Slag.								
	0.	4.	8.	12.	16.	20.	30.	40.	50.
Acid open-hearth . .	36	35	33	33	33	30	26	20	13
Blast furnace . . .	36	33	32	29	20	14	14	14	10
Basic open-hearth . .	36	33	32	20	14	12	11	10	10
Heating furnace . .	36	34	32	31	29	20	15	11	9

The resistance of bauxite bricks to the action of slags is probably due in some measure to the action of alumina in increasing the viscosity of any molten mass or slag containing it, and therefore rendering such slag less active than would otherwise be the case.

Zirconia bricks are very resistant to the action of slags, both acid and basic, and consequently are valuable as a refractory material. According to *Mineral Foote-Notes*, zirconia bricks withstand the corrosive action of (*a*) acid slags containing manganous and ferrous oxides, such as bessemer converter slags, puddling furnace slags ; (*b*) glass of various kinds ; (*c*) cobalt nickel speiss ; (*d*) ladle slags which are not basic. The following substances attack zirconia moderately : (*a*) basic ladle slags, (*b*) iron oxide, (*c*) copper oxide, (*d*) portland cement, (*e*) litharge. The following substances attack it rapidly : (*a*) iron sulphide, (*b*) sodium carbonate, (*c*) sodium hydroxide, (*d*) fluorspar or cryolite.

Carbon, chromite, and carboxide bricks are very inert to chemical action, and are highly resistant to slags and fluxing agents.

Table CXXX shows the effect of various proportions of different slags on the refractoriness of chromite bricks as determined by Howe, Phelps, and Ferguson.

TABLE CXXX.—*Effect of Slags on Chromite Bricks*
(*The Results are expressed in Seger Cones*)

Type of Slag.	Percentage of Slag.							
	4.	8.	12.	16.	20.	30.	40.	50.
Acid open-hearth .	36	33	31	30	20	15	13	12
Blast furnace . .	..	..	35	34	32	16	9	8
Heating furnace . .	..	..	..	..	36	35	36	36

Carborundum is attacked slowly at a bright-red heat by sodium carbonate, caustic soda, and sodium peroxide, whilst red lead attacks it rapidly. Carborundum bricks are not attacked by either silica or molten iron separately, but when together a corrosive action takes place. The bricks are attacked by slags to a greater extent in an oxidising atmosphere than under reducing conditions.

Measurement of Corrosion.—The American Society for Testing Materials has suggested that the resistance of refractory materials to corrosion may be tested by drilling a hole $2\frac{1}{2}$ inches diameter and $\frac{1}{2}$ inch deep into the sample, which is then heated to a temperature of 1350° C. in not less than five hours, and 35 grams of powdered slag are introduced, the temperature being maintained for two hours. The furnace is then cooled and the brick cut vertically so as to show the depth of the penetration.

Another method for a slagging test on refractory materials adopted by the

American Society for Testing Materials,[1] suggests that 35 grams of slag should be ground to 30-mesh and placed in a refractory ring in contact with the brick, which is heated to 1350° C. and maintained at that temperature for two hours. The brick is then cooled, cut, and the area of penetration measured. The slag suggested has the following analysis :—

	Per cent.
Silica	19·00
Alumina	12·89
Ferric oxide	15·73
Lime	33·50
Magnesia	6·93
Manganese oxide	3·52
Soda	8·50

The melting-point of the slag is about 1270° C.

The corrosion test suggested by the committee of the English Ceramic Society [2] is very similar to the last-mentioned method.

G. H. Brown [3] objects to the customary method of placing the slag in a depression in a firebrick or in a cell cemented on to the brick, and prefers to place the bricks on end in fireclay boxes each 9 inches × 8 inches × 3 inches internally, and burned at Cone 12 before use. The bricks are packed on two sides with finely ground slag, and the boxes with their contents are burned in a down-draught kiln reaching 1400° C. in thirty-six hours, reducing conditions being maintained during the last twelve hours. In this manner, a considerable portion of the brick is subjected to the action of the slag and structural defects are readily detected. The use of so large an amount of slag reduces errors due to changes in its composition and facilitates a study of the time effect. He found that the slag prepared from coal ash and also a synthetic mixture of similar composition vigorously attacked a silica brick and a bauxite one, penetrating to the centre and producing a honeycomb structure. A magnesite brick showed penetration to the centre and considerable solution at the surface, whilst a carborundum brick showed no penetration, but excessive surface solution. Some brands of clay bricks were not attacked at all, but others, which were underburned or containing coarse grog, were irregularly penetrated.

The depth of penetration is not always an important measure of the harmfulness of a slag, as basic slag may penetrate deeply and yet not corrode seriously, whilst lime, though it may not penetrate far, forms a very corrosive slag and is, therefore, much more harmful.

The results of a test in which a small quantity of slag is placed in a cavity in a brick and heated do not always agree with those experienced in working on a large scale, because in the test the penetration is complete in about two hours, but in a large furnace, owing to the much larger quantity of slag present, the penetration may continue until the brickwork is destroyed. The amount of slag used in the test

[1] *Amer. Soc. for Testing Mtls.*, **20**, I., 620–23 (1920).
[2] *Trans. Eng. Cer. Soc.*, **18**, 516 (1918–19).
[3] *Trans. Amer. Cer. Soc.*, **18**, 277–81 (1916).

also affects the results. R. M. Howe [1] having found that by using 105 grams instead of 35 grams of slag, the penetration was increased by 19 per cent.

The atmosphere of the furnace during the slag test also has an important influence on the penetration, some slags being more active under oxidising than under reducing conditions, and *vice versa*.

It is also desirable to make slag-tests at a temperature approximating to that of the furnace at which the bricks are to be used, as a small difference in temperature may cause a very large difference in the amount of corrosion or penetration. Thus, R. M. Howe found that a slag melting at 1050° C. only penetrated a firebrick to a depth of 0·02 inch at 1150° C., but at 1450° C. the penetration was 0·79 inch. Similarly, a zinc-slag penetrated a firebrick 0·04 inch at 1150° C., and 0·32 inch at 1450° C., the melting-point of the slag being 1025° C.

A further source of error pointed out by R. M. Howe is that the difference between the penetration due to the porosity of the brick and that due to chemical action is not shown, yet it is very important, as penetration due to porosity does not reduce the strength, whilst corrosion rapidly weakens and may eventually destroy the brickwork. For this reason, a large penetration due to porosity may do far less harm than a much smaller penetration due to chemical action in a denser brick. The results obtained by R. M. Howe and shown in Table CXXXI, show that there is no definite relation between the slag-penetration and the durability of the bricks in actual practice, as the hand-made bricks, though showing a large penetration due to its porosity, gave better service than a denser brick showing no penetration in the test.

TABLE CXXXI.—*Comparison of Slag Test and Durability*

Texture of Bricks.	Process of Manufacture.	Refractoriness. Cone.	Slag Penetration.	Durability in Use.
Fine . .	Steam press	31	0·29	Fair.
Medium . .	Hand-made	32	0·52	Very good.
Medium . .	Steam press	32	0·00	Very good.

A further difference between slag-tests, in which the slag is placed in a depression or cavity in the bricks and the effect of slag in actual furnace-working, which prevents any accurate comparison, is that, in actual use, the slag only attacks one surface of the brick, and that portion of the brickwork is only heated to a very small depth, whilst in a slag-test the brick is heated throughout to the same temperature. Consequently, in the test the slag will penetrate the brick to a much greater extent in a given time than it would do in actual use, because in the latter it would soon reach a cooler part of the brickwork and would then become viscous or even solid, and so

[1] *J. Amer. Cer. Soc.*, **6**, 406 (1923).

would cease to corrode the brickwork until the surface of the brick was worn away by the solution or abrasion of its hottest face.

R. M. Howe, S. M. Phelps, and R. F. Ferguson [1] suggest that the best method of testing the resistance of refractory materials to the action of slag is to powder the bricks and slag to be tested so that they will pass completely through an 80-mesh sieve, mix them in various proportions, and determine the refractoriness of the mixtures. They claim that this method more nearly agrees with the conditions observed in works' practice, the chief of these being (*a*) increased intensity of action with increased slag concentration; (*b*) the different action of different slags; and (*c*) the effect of any slag differs with different refractory materials.

Chemical Reactions occurring at Lower Temperatures

The chemical reactions to which ceramic materials are subjected at ordinary temperatures are chiefly due to (*a*) water, (*b*) acids, and (*c*) alkalies.

Water has no rapid effect upon most ceramic materials at ordinary temperatures, with the exception of certain metallic oxides such as lime, magnesia, and calcined dolomite, which are hydrolysed more or less rapidly by it. Lime is the most rapidly attacked and magnesia least, dolomite being intermediate, as might be anticipated from its composition, the lime in the dolomite being most rapidly converted. The effect of water may be reduced to a great extent by adding a small proportion of clay, iron oxide, or other fluxes, calcining the materials at a temperature sufficiently high to fill all the pores and coat all the particles with a glassy film of silicate or spinel. Some bricks composed of calcium and magnesium silicates and aluminates develop hydraulic properties, and if present in burned dolomite may absorb water and cause disintegration of the calcined mass. Campbell [2] found that two calcium ferrates ($5CaO3Fe_2O_3$ and $6CaO3Fe_2O_3$) also develop hydraulic properties.

Caustic magnesia is very soluble in water, and still more so in slightly acidified water, such as that containing carbonic acid, but magnesia bricks made of a much more intensely calcined magnesia are practically insoluble in water or dilute acids, except on very prolonged exposure. On the other hand, they are very rapidly attacked by steam, so that they must not be brought into contact with this vapour or they will be rapidly disintegrated (see also *Corrosion*, p. 494).

Most *silicates*, when subjected to the action of water for a long period of time, become more or less hydrolysed, but the action is very slow. This is described under *Weathering* (p. 506).

Hydrochloric acid attacks many calcareous and ferruginous substances, including dolomite, magnesite, calcite, iron oxides, etc., olivine, serpentine, chlorite, nepheline, epidote, leucite, and apatite; some other phosphates, monazite, etc., are attacked to some extent. Some sulphides are also dissolved.

Calcined china clay and calcined halloysite differ from one another in that the latter can be completely dissolved in hydrochloric acid. Raw bauxite is readily

[1] *Loc. cit.*, p. 495.

[2] *J. Ind. Eng. Chem.*, **11**, 116–20 (1919).

attacked and completely dissolved by hydrochloric and sulphuric acids. When intensely calcined, however, it is practically insoluble. This is due probably to polymerisation, which appears to occur at about 900° C.

Sulphuric acid when hot and concentrated attacks clays and other hydrated alumino-silicates and also most basic materials. When clay is heated for a long time with concentrated sulphuric acid the clay is decomposed, possibly with the separation of silica and the formation of aluminium sulphate.

Nitric acid behaves in a similar manner to hydrochloric acid. In addition, it decomposes sulphides forming nitrates.

Phosphoric acid attacks silica glass and many silicates at temperatures above 400° C., forming the corresponding phosphates and liberating silica. Calcined and crystalline silica is not attacked by phosphoric acid below 300° C., but precipitated silica is attacked at lower temperatures.

Phosphoric acid also combines with silica to form a crystalline substance having the formula $SiO_2P_2O_5$, this substance occurring in four allotropic forms, two of the low-temperature forms being attacked by water rapidly, whilst the other two, which are stable at high temperatures, are insensitive to water or acids, even hydrofluoric. The resistance of siliceous glasses containing phosphoric acid to hydrofluoric acid is due to the formation of $SiO_2P_2O_5$, which is not affected by any acids.

Hydrofluoric acid decomposes many siliceous minerals which are unaffected by other acids, silicon fluoride being volatilised. Schwarz [1] found the following amounts of various kinds of silica to be dissolved by 1 per cent. solution of hydrofluoric acid in one hour at 100° C. :—

Quartz	5·2 per cent.
Tridymite	20·3 ,,
Cristobalite	25·8 ,,
Gelatinous silica	52·9 ,,

According to Gautier and Clausmann, silica glass is only one-tenth as soluble in hydrofluoric acid as ordinary glass.

The action of carbonated water (which is dilute *carbonic acid*) is, in some cases, comparatively rapid, as the action of rain water upon limestone, basalts, and olivine (see *Weathering*, p. 506).

Silica is very resistant to all acids, except hydrofluoric acid and phosphoric acid at high temperatures.

W. Ostwald considers the difference in solubility of different forms of silica to be due to their different degrees of dispersion (see p. 11), quartz being the least dispersed and, therefore, least soluble.

Carborundum is slightly attacked by hydrofluoric acid, but not to any great extent. Crystolon is only attacked by hydrofluoric acid, but it is decomposed readily on heating with alkalies and alkaline carbonates, and it is also attacked at red heat by most metallic oxides. Siloxicon is decomposed by hydrofluoric acid. Silundum, however, is quite unaffected by it.

[1] *Z. Anorg. Chem.*, **76**, 422 (1912).

Alkalies usually combine with acid substances, but their action in the cold upon silicates and alumino-silicates is slight, and it is very feeble in the case of crystalline silicates. Freshly precipitated hydrated silica is readily soluble in alkaline solutions. Flint is readily soluble in alkaline solutions at 200° C., this fact being used in one method of making sodium silicate.

Mylius and Meusser found the following amounts of silica glass to be dissolved from surface of 14 square inches by various hot solutions of alkaline hydrates and carbonates :—

TABLE CXXXII.—*Solution of Silica Glass by Alkalies*

Temperature, ° C.	Time of Contact.	Reagent.	Concentration.	Loss in m.gms.
18	2 days	Ammonium hydrate	10 per cent.	0·8
		Sodium hydrate	10 ,,	0·4
		Potassium hydrate	30 ,,	1·2
18	14 days	Sodium hydrate	1/N	2·0
		Sodium carbonate	1/N	0·6
		Barium carbonate	Saturated sol.	0·0
		Acid sodium phosphate	,,	0·0
100	3 hours	Sodium hydrate	2/N	33·0
		Potassium hydrate	2/N	31·0
		Sodium carbonate	2/N	10·0

Silica reacts with some bases at a moderate temperature in the presence of steam. Use is made of this fact in the hardening of sand-lime bricks, the calcium silicate produced acting as a bond for the particles of sand. The following actions may occur :—

$$Ca(OH)_2+SiO_2=CaOSiO_2H_2O,$$
$$CaOSiO_2H_2O+Ca(OH)_2=2CaOSiO_2+H_2O,$$
$$Ca(OH)_2+2SiO_2=CaO2SiO_2H_2O.$$

The briquetting of ores with lime, soda, and water-glass are similar instances of the action of alkalies upon silica in the presence of water.

Alkalies do not greatly affect silica in the absence of water below a temperature of 1000° C., but if heated to a higher temperature it is attacked slowly and converted into fusible silicates.

The effect of reagents on most ceramic materials is not usually very distinct on account of the heterogeneous nature of the latter and the limited extent to which they may be attacked. No one substance can usually be separated from the rest by chemical reagents, as before one is completely dissolved another will have begun to decompose.

Weathering

Exposure to weather has both chemical and physical effects on ceramic materials. The chief chemical actions which occur are :

(*a*) The solution and replacement of some substances after oxidation and hydrolysation.

(*b*) The oxidation of carbonaceous matter, sulphides, and some ferrous compounds.

(*c*) The hydration or hydrolysis of substances which are ordinarily insoluble.

Solution and replacement by water has an important effect in changing the chemical nature of rocks through which it percolates, especially when it contains dissolved substances in solution. Thus, the percolation of water containing carbon dioxide through clay beds may cause the solution and removal of any soluble substances present. For instance, calcium carbonate may be removed in this way from a highly calcareous clay or clayey limestone, and it is generally thought that the pocket clays of Derbyshire are composed of the insoluble residuum from a clayey limestone, the greater part of which has been removed by the solution of the calcium carbonate. Some clay beds containing calcium carbonate are richer in this impurity near the bottom of the bed than at the top, this latter portion having been partially purified by carbonated water descending from the surface and dissolving the calcium carbonate in its passage.

Even silica—though normally regarded as insoluble in water—is not wholly so. On the contrary, there are many rocks which owe their great strength to the precipitation in them of silica which was previously dissolved in the water percolating through them.

The disintegration of rocks and clay beds by weathering is largely, though not wholly, due to the removal, in solution, of soluble substances originally present as the bonding material.[1]

Conversely, water containing silica in solution, when in contact with siliceous rocks, tends to permit the precipitation of the silica in the pores of the rock, with the result that the particles of aggregate are still more firmly united with a siliceous cement. As water can contain both silica and calcium bicarbonate simultaneously in solution, a limestone may have part of its calcium carbonate removed in solution by percolating waters and replaced by silica—chiefly in the form of chert. Thus, near Carlow, in Ireland, a bed of chert 30 to 40 feet thick has replaced the original Carboniferous Limestone. The flints and chert in some English chalk and limestone beds are due to metasomatic replacement of this character. Sometimes quartz is replaced by calcite brought in solution by percolating waters, but this type of replacement is not common.

Another typical rock formed by partial replacement is dolomite, which has been formed by the replacement of some of the calcium carbonate in limestones by magnesium carbonate. Some dolomites, however, appear to have been produced by simultaneous crystallisation of both magnesium and calcium carbonates.

Weather has a bleaching action on clays and some other minerals containing

[1] The physical actions which occur during weathering are described on p. 253.

suitable carbonaceous matter, as the latter, when decomposing as a result of exposure to air and water, forms humic and other acids which dissolve some of the iron and other compounds (p. 107) and remove them in solution.

Prolonged exposure to the weather also results in the solution and removal of selenite and gypsum. Any other soluble salts in a clay or other ceramic material may also be dissolved and carried away by water percolating through the mass.

Cementation, or the binding of the particles of aggregate into a strong mass of rock by means of a binding agent or " cement," is caused, according to Hatch and Rastall, by (*a*) the mingling of solutions from different sources, as when a solution containing oxygen comes into contact with one containing iron compounds in solution, the result being the precipitation of iron oxide and the cementation of the rock in which the precipitation occurs ; (*b*) the chemical reactions which occur between rocks and solutions percolating through them. Thus, the action of water upon anhydrous rocks causes the formation of hydrates or hydroxides, which fill up the pores and cement the rock-particles. Thus, felspar may be replaced by zeolites or hæmatite by limonite. Temperature and pressure play an important part in modifying the effect of chemical reactions in cementation.

Oxidation.—Exposure to weather (*i.e.* to water and air) converts ferrous compounds into the ferric state, limonite being the chief product. Iron sulphides are, to some extent, converted into sulphates, marcasite being more readily oxidised than pyrites. Copper sulphides are oxidised in a similar manner, erubescite being readily broken down and chalcopyrite with more difficulty.

Sunlight appears to favour oxidation and has, therefore, an important influence on the weathering of clays. Remarkable differences in the character of some clays occur after even a few hours to sunlight and air, whilst other clays are scarcely affected. The difference is, apparently, due to some oxidation processes, possibly associated with colloidal changes accompanying the hydration of the material ; but the precise nature of these changes can only be surmised, as they have not been fully investigated.

Hydration or **hydrolysis,** which consists in the addition of one or more molecules of water to a substance, is an important result of weathering. It is really the reverse of the neutralisation of an acid by a base, and may be expressed by the equation :

$$\underset{\text{acid}}{(\text{acid radical}+\text{H})}+\underset{\text{base.}}{(\text{basic radical}+\text{OH})}$$

$$\text{salt}+\text{water}=\qquad\qquad +$$

Thus, in hydrolysis, a salt splits up, forming an acid and a base or, occasionally, a basic salt. The duration of the exposure to water and the enormous masses involved enable changes to take place which cannot be accomplished in the chemical laboratory, with the result that most silicates and oxides can be hydrolysed and compounds, such as clays, formed, which cannot be produced by any artificial means.

In the same way, the hydrolysis of iron compounds in clays and other rocks sometimes results in the formation of a particularly strong ferruginous cement.

The yellow films or stains widely distributed among rocks are due to the production of limonite (p. 418) by the oxidation and hydrolysis of other iron compounds.

CHAPTER XII

HEAT AND TEMPERATURE

The application of heat is the chief means by which bricks and other articles made of clay and other ceramic materials are converted from the friable or pasty state into hard, strong solids possessing other valuable properties. A knowledge of the principal effects of heat on such materials is, therefore, of great importance to those concerned in the manufacture and use of clay and allied substances, as well as of various refractory materials.

In dealing with heat and its effects it is necessary to avoid all confusion of thought with respect to the terms " heat " and " temperature."

Heat is the property possessed by all matter of creating a certain well-known sensation in the nerves, by means of which the substance is recognised as hot, warm, cool, or cold. Heat is caused by the motion of the molecules of which all matter is composed, and it may be transferred from one body to another, either by direct contact or through a third body. The true conception of heat was not understood until comparatively recently, and many expressions are employed which suggest that heat is a form of matter instead of a result of molecular motion. Hence, heat is said to be " absorbed," " evolved," " conducted," " passed," " held," " contained," and though these terms are not strictly accurate, they are accepted and in common use. Care should, however, be taken that their use does not lead to an erroneous idea of the nature of heat.

The measurement of heat is termed *calorimetry*.

Temperature is a term denoting the thermal condition of a body as regards its power of transmitting heat to or receiving heat from other bodies. Thus, whilst one body which is twice the volume of another similar body under identical conditions may be said to contain twice as much heat, the temperature of both bodies is the same. If, however, the smaller body contains the same amount of heat as the larger one, the temperature of the small body would be higher. If, for example, the heat released on burning 1 lb. of coal (about 14,000 heat units) could be transferred to 40 lb. of silica, the temperature of the latter would be raised to 1000° C., *i.e.* to a bright-red heat. The idea of temperature is allied to that of intensity and not of quantity, so that when a substance is at a higher temperature than another, it appears to be hotter, though the total quantity of heat may be the same. Similarly, the quantity of water in two tanks of equal size may be the same, but if one tank is 100 feet above the other the water will be delivered from the higher tank at a much greater pressure. Hence, temperature bears a similar relation to the quantity of heat in a substance as the " head " or pressure of water or steam bears to its volume.

If two masses are at the same temperature there will be no passage of heat from one to the other, because they are in a state of thermal equilibrium. When the state of equilibrium is disturbed, however, heat will pass from one to the other until equilibrium is again restored. Here, again, the analogy with the pressure and volume of water is applicable ; if the water is at the same level in two vessels no flow of water will occur, but if the water in one vessel is at a higher level than that in the other, water will flow into the lower vessel until the level in both is the same.

If heat is conceived in terms of the motion of the molecules of a substance, temperature may be conceived as due to the intensity or rapidity of the molecular movement.

The temperature of a substance is dependent upon (*a*) the amount of heat ; (*b*) the mass and volume of the substance ; and (*c*) the nature of the substance.

The measurement of temperature is termed *thermometry* or *pyrometry* ; the former term is used for temperatures between about −30° C. and 300° C. (*i.e.* for temperatures for which a thermometer can be used), and the latter for these and also for other temperatures for which a pyrometer is employed. The two chief scales of temperature are the Fahrenheit and Celsius or Centigrade scales respectively ; they are described in the section on *Temperature Measurement.*

Heat Measurement.—In order to compare the quantities of heat in different bodies it is necessary to have a unit of heat. Unfortunately, there are three units in use, two being employed mainly for accurate scientific work and one in industry. The two former are based on the metric system and are termed the *major* and *minor calorie* respectively, whilst the third is in English measure and is termed a *British Thermal Unit* (commonly abbreviated to B.T.U.).

A *minor calorie* [1] is the amount of heat required to raise the temperature of 1 gram of water 1° C. (strictly from 0°–1° C.) at atmospheric pressure. A *large* or *major Calorie* is the amount of heat required to raise 1 kilogram of water 1° C. at atmospheric pressure, and it is, therefore, one thousand times as large as the calorie.

A *British Thermal Unit* is the amount of heat required to raise 1 lb. of water 1° F. (strictly from 32°–33° F.) at atmospheric pressure.

Another unit sometimes used is termed the *Centigrade unit*, often erroneously termed a calorie ; it is the amount of heat required to raise 1 lb. of water 1° C. at atmospheric pressure.

Ostwald has pointed out that, in the case of chemical reactions, the calorie is not wholly satisfactory as a unit of heat in dealing with the heat of reaction, and he prefers to use the mechanical equivalent, which represents the energy expended or " work " done in bringing about the reaction. The mechanical equivalent of heat was first investigated by Joule, who found that one calorie is equivalent to 41,800 gm.-cms., or 41,800,000 ergs [2] or 4·18 joules.[3] Thus, the conversion of ice into liquid

[1] Usually spelt with a small *c* to distinguish it from the major Calorie which is spelt with a capital *C*.

[2] An *erg* is equivalent to the work done when a force of 1 dyne is overcome through a distance of 1 cm., a *dyne* being the force which, acting on 1 gm. for 1 second, gives it a velocity of 1 cm. per sec.

[3] A *joule* is equivalent to 10,000,000 ergs, and a *kilo joule* (=J), to 1000 joules.

water at the same temperature requires 6·0 J or 1434 calories, whilst the condensation of steam to liquid water at the same temperature evolves 40·5 J or 11,745 calories.

The following factors are useful in converting heat values into energy values :—

B.T.U. to calories	multiply by 0·252
B.T.U. to joules	,, ,, 1055
B.T.U. to foot-pounds	,, ,, 777
B.T.U. to watt-hours	,, ,, 0·293
B.T.U. per cubic foot to calories per c.c.	,, ,, 8·90
B.T.U. per lb. to calories per kilo.	,, ,, 0·556
Calories to B.T.U.	,, ,, 3.968
Calories to joules	,, ,, 4·18
Calories per c.c. to B.T.U. per cubic foot	,, ,, 0·1124
Calories per kilo. to B.T.U. per lb.	,, ,, 1·8
Kilo joules to Calories	,, ,, 239

The quantity of heat in an article or in a given weight of material is measured by means of a calorimeter, the method usually adopted being that known as the " method of mixtures." This depends on the fact that if two substances are at different temperatures, the hotter one will transfer heat to the cooler one until both attain the same temperature. The calorimeter used primarily consists of a vessel containing a known quantity of water into which the hot sample is placed, and to which it imparts heat until both the sample and the water are at the same temperature, the distribution of heat being aided by stirring the water. By measuring the temperature of the water before and after the immersion of the sample, the amount of heat in it can be calculated as described in the following section. Calorimeters of various special designs are used for accurate work, as it is very important to reduce all loss of heat by radiation, etc., to a minimum. The measurement of conducted heat is dealt with on p. 515.

Thermal Capacity

In accordance with the conception of heat as a form of matter (p. 508), various materials appear to have different capacities for heat, *i.e.* equal masses of different substances which are all at the same temperature will require to absorb different quantities of heat before they are all raised to a given higher temperature. This apparent ability to " contain " heat is due to an incorrect understanding of its nature, but such a conception is so convenient that it is in common use. Hence, the apparent ability of a substance to absorb and retain heat is termed the thermal capacity of that substance, and in order to compare the thermal capacities of different substances a standard of measurement is used, termed the **specific heat**, which may be defined as the amount of heat required to effect an increase of one degree in the temperature of a unit mass of the substance under a definite pressure (usually one atmosphere). For convenience, the specific heat of water is assumed to be unity, and other substances are expressed in relation to this.

The specific heat depends on whether the substance is in the crystalline or glassy

state, or, if the former, what is its crystalline form and internal molecular arrangement. Thus, crystalline quartz has a specific heat of 0·185 between 12° and 100° C., whilst the specific heat of amorphous silica (opal) between 12° and 100° C. is 0·2375.

The effect of heat or temperature on the specific heat of various substances is considered in Chapter XIII.

The specific heat is not constant at all temperatures, so that it is necessary to specify the particular rise in temperature employed in the definition; this may be from 0°–1° C., 32°–33° F., 60°–61° F., or any other convenient range near atmospheric temperature. For special purposes, the specific heat at other temperatures may require to be determined, in which case the temperature should be specified in any statement of the results.

The specific heat is usually fairly constant between 10° C. and 200°–300° C., but boron, carbon, and silicon are exceptions, and vary very greatly between these temperatures. At higher temperatures the specific heat of ceramic materials increases somewhat more rapidly than the corresponding rise in temperature (Chapter XIII).

Vogt has stated that the specific heat at different temperatures may be calculated from the formula :

$$C_t = C_o(1 + 0{\cdot}000078t),$$

where C_t is the specific heat at temperature $t°$ C., and C_o is the specific heat at 0° C.

The specific heat of substances is generally greater when they are in the liquid than in the solid and gaseous states.

Table CXXXIII shows the specific heat of various substances :—

TABLE CXXXIII.—*Specific Heats*

Element.	Specific Heat of Equal Masses.	Element.	Specific Heat of Equal Masses.
Sulphur	0·1776	Iodine	0·0541
Magnesium	0·2499	Bromine (solid)	0·0843
Zinc	0·0955	Potassium	0·1655
Aluminium	0·2143	Sodium	0·2934
Iron	0·1138	Arsenic	0·0830
Nickel	0·1070	Antimony	0·0523
Cobalt	0·1067	Bismuth	0·0305
Manganese	0·1217	Silver	0·0570
Tin	0·0548	Gold	0·0324
Copper	0·0952	Carbon at 980°	0·4580
Lead	0·0314	Boron at 600°	0·5000
Mercury (solid)	0·0319	Silicon at 232°	0·2020
Platinum	0·0324		

A *determination of the specific heat* of a substance is usually made by means of the method of mixtures (p. 510), by heating a weighed quantity of the substance to the required temperature for some time until it is uniformly heated. It is then quickly transferred to a suitable calorimeter containing a weighed quantity of cold water at a known temperature, and the latter is stirred so as to distribute the heat. The temperature of the water is noted at intervals of half a minute or so, until a constant temperature is reached. The specific heat is then calculated from the following formula :—

$$\text{Specific heat} = \frac{W_2 \times (T_3 - T_2)}{W_1 \times (T_1 - T_3)}$$

where

W_1 is the weight of the substance in grams.
W_2 is the weight of the water in grams.
T_1 is the maximum temperature of the substance.
T_2 is the original temperature of the water.
T_3 is the final temperature of the water.

The above formula is based on the assumption that the quantity of heat in the substance at the given temperature is W_1T_1s, where W_1 and T_1 have the same significance as in the formula and s is the specific heat at the temperature T_1.

The heat in the water prior to the determination is W_2T_2, and after the determination it is W_2T_3, and as the whole of the heat lost by the substance is assumed to be transferred to the water $W_1(T_1-T_3)s=W_2(T_3-T_2)$.

For the same reason, the total heat lost by the substance in passing from the temperature T_1 to T_3 is $W_2\ (T_3-T_2)$.

Where accurate results are required, a special calorimeter must be used and numerous precautions taken to avoid the loss of heat by radiation. This is especially necessary in the case of substances having a low thermal conductivity, which take a considerable time before they are cooled to a constant temperature.

The **atomic heat** of a solid substance is the product of its specific heat and atomic weight, and it has been found by Dulong and Petit that for elementary substances the atomic heat is nearly constant, viz. 6·2–6·3, though this does not appear to apply to some elements with atomic weights of less than 40. According to more recent investigations, 5·9 is a more reliable figure for the atomic heat at constant volume, as shown in Table CXXXIV, due to E. B. Millard.[1]

Boltzmann [2] has shown that the atomic heat can be directly deduced from the classical Kinetic theory, and that the constant of Dulong and Petit should be $3R=5{\cdot}97$ calories per degree. Lewis [3] states that the atomic heat of extremely electropositive metals (with atomic weight below 40) is irregular, because certain electrons in them are held so feebly that they acquire thermal energy apart from that of the atoms.

[1] *Physical Chemistry for Colleges* (M'Graw-Hill Book Co., 1921).
[2] *Sitzb. Kgl. Akad. Wiss. Wien.*, **63** (2), 679 (1871).
[3] *J. Amer. Chem. Soc.*, **29**, 1165, 1516 (1907).

TABLE CXXXIV.—*Atomic Heats of Various Elements at Constant Volume and Pressure*

Element.	Atomic Heat at Constant Volume.	Atomic Heat at Constant Pressure.	Element.	Atomic Heat at Constant Volume.	Atomic Heat at Constant Pressure.
Sodium . .	6·4	6·4	Cadmium .	5·9	6·2
Magnesium .	5·8	6·0	Tin. . .	6·1	6·4
Aluminium .	5·7	5·8	Antimony .	5·9	6·0
Potassium .	0·5	7·1	Iodine . .	6·0	6·9
Iron . .	5·9	6·0	Platinum .	5·9	6·1
Nickel . .	5·9	6·1	Gold . .	5·9	6·2
Copper . .	5·6	5·8	Thallium .	6·1	6·4
Zinc . .	5·6	6·0	Lead . .	5·9	6·3
Palladium .	5·9	6·1	Bismuth . .	6·2	6·3
Silver . .	5·8	6·1			
			Average .	5·9	6·2

The atomic heats at constant volume of the principal elements having a low atomic weight are shown in Table CXXXV, which is also due to E. B. Millard.

TABLE CXXXV.—*Irregular Atomic Heats*

Substance.	Atomic Heat at Constant Volume.	Substance.	Atomic Heat at Constant Volume.
Sulphur . .	5·5	Silicon . . .	4·8
Phosphorus . .	5·6	Aluminium . .	5·7
Carbon (diamond) .	1·6	Oxygen . .	4·0
Carbon (graphite) .	1·9	Hydrogen . .	2·3
Boron . . .	2·5		

The atomic heat of elements decreases rapidly at low temperatures and increases slightly at higher temperatures.

According to M. Born and E. Brody,[1] the atomic heat at different temperatures (at constant volume) is $5{\cdot}8546+0{\cdot}000649t$.

The **molecular heat** has been studied by Regnault, who found that the specific

[1] *Z. Physik*, **6**, 132–9 (1921).

heats of compound bodies possessing similar chemical formulæ are inversely proportional to their equivalents ; conversely, equivalent quantities of compound bodies possessing similar atomic composition possess also the same specific heat. According to Kopp and Woestyn, the molecular heat of compounds is $n \times 6{\cdot}4$, where n is the number of molecules. Thus, a solid compound consisting of one atom of one solid plus two atoms of another solid will have a molecular heat of about 19·2 calories per formula weight. The heat capacity of solids which consist of elements which at ordinary atmospheric temperatures are gases or form combinations which do not conform to Kopp's law, have molecular heats less than that of compounds formed from elements which are solid at ordinary temperatures. This law is not reliable.

The Transmission of Heat

The transmission of heat from one body to another may be effected in various ways :—

(*a*) By **conduction**, in which the heat is transferred by molecules of the hotter substance bombarding those of the cooler substance and so setting up a corresponding motion amongst the molecules in the latter, which were moving less rapidly, the acceleration of motion progressing at a definite rate through the second substance. The rate at which the heat passes through a material—as measured by the rise in temperature of the latter—is termed *thermal conductivity.*

As a result of their different molecular structure, materials have different powers of conducting heat. Most metals have a higher thermal conductivity than non-metals or compounds, *i.e.* they conduct heat rapidly through their mass. Ceramic materials are, on the whole, very poor conductors of heat, though some, such as carborundum, have a higher thermal conductivity than others.

Factors Influencing Thermal Conductivity.—The chief factors to be considered in connection with the rate of passage of heat through ceramic materials are :—

(*a*) The chemical composition of the material used.
(*b*) Its previous heat treatment.
(*c*) The texture or physical condition of the material.
(*d*) The porosity of the material.
(*e*) The temperature at which the material is used or tested.

Materials differ with regard to their thermal conductivity, which also changes with the heat-treatment to which they have been subjected, just as the temperature and duration of firing during manufacture modifies other properties of such materials. It is also important to know the condition of the material during use, as the thermal conductivity of a brick or block may be quite different from that of the same substance when in the powdered state. Thus, magnesia when in the form of a refractory brick is a moderately good conductor of heat, whilst in the form of a powder it is extremely resistant to heat and has a high insulatory value, as will be seen in Table CLXXVIII.

The influence of texture and porosity may be considered together, as the principal effect on the thermal conductivity is due to the relation between the amount of solid and of air which the heat has to traverse in passing through the material. As air is a much better insulator than any solid material, the larger the proportion of air the greater will be the thermal insulating power of the material. Hence, a fine-grained, close-textured material has a much greater thermal conductivity than one with a coarser open texture. The relation between insulating power and texture or porosity cannot, however, be expressed in very simple terms, as it is modified by (*a*) temperature, (*b*) the size and (*c*) the shape of the pores or interstices, (*d*) the position of the interstices relative to each other and to the solid matter.

If the rate of radiation increases until it equals the rate of conduction through a solid the pore-spaces will cease to act as insulators. With pores 0·01 cm. diameter this equality of heat-transfer occurs, according to Dougill, Hodsman, and Cobb,[1] at 3600° C. At lower temperatures, or with wider pores, the rate of radiation is lower than that at which the heat passes through the solid material, so that the presence of pores in materials used at any temperature ordinarily attainable decreases the thermal conductivity. A. T. Green[2] has, however, stated that at much lower temperatures (*e.g.* 1400°–1500° C., and even at 1150° C.) some of the pore-spaces lose their insulating properties and transmit heat at nearly the same rate as the solid matter. If this statement is correct, pore-spaces in ceramic materials do not have so great an insulating power at high temperatures as is usually assumed.

In comparing the thermal conductivity of different substances, the unit is the amount of heat which passes in one second through a mass of the material of unit thickness and area when the difference in temperature of opposite faces is one degree. If the C.G.S. unit is adopted the thermal conductivity will be expressed as gram-calories per second per centimetre-cube for a difference of 1° C. This can be converted to the British Unit, viz. B.T.U. per second per 1 inch cube, by multiplying the conductivity in C.G.S. units by 8·672.

The reciprocal of thermal conductivity or resistance offered by unit mass of a substance to the passage of heat is termed its *resistivity*.

The thermal conductivity of a solid substance, such as a ceramic material, is usually determined by exposing one face to a constant source of heat and measuring the temperature at opposite faces, or at the hot face and at a point in the material a convenient distance from it. The greatest source of error occurs in applying the heat uniformly to the hot face and ensuring its uniform distribution through the material to be tested, so the various methods which have been devised for determining the thermal conductivity differ chiefly in the means used to avoid this source of error.

In Wologdine's method, the test-pieces are in the form of round flat plates, 160 mm. (6·4 inch) diameter and 50 mm. (2 inch) thick. Holes are pierced to depths of 5 mm. (0·2 inch), 45 mm. (1·8 inch), and 50 mm. (2 inch) from the upper surface and thermo-couples attached to pyrometers inserted in them. The lower surface of the

[1] *J. Soc. Chem. Ind.*, **34**, 465 (1915).
[2] *Trans. Eng. Cer. Soc.*, **21**, 394 (1921–22).

test-piece is heated in a gas-furnace and the heat passing through it is measured by a water-calorimeter, whilst the temperature at each of the levels above mentioned is read at intervals.

The thermal conductivity may be calculated from the formula :—

$$Q = \frac{P(t_2 - t_1)}{60}$$

where Q is the quantity of heat traversing per second an area equal to that of the base of the calorimeter, t_1 and t_2 the temperatures of the water entering and leaving the calorimeter, and P the quantity of water passed in grams per minute. The coefficient of thermal conductivity is $\frac{S(T_5 - T_0)}{QL}$, where S is the area of the bottom in square cm., L the thickness of the plate in cm., and T_0 and T_5 the temperatures of the upper and lower surfaces.

Various modifications of Wologdine's method have been devised in order to lessen the error possible. Goerens [1] used a " guard ring " consisting of an outer jacket through which water flows continuously, and his thermo-couples were arranged to run parallel to the hot face. Dougill, Hodsman, and Cobb [2] used a second calorimeter to surround the first one, but the value of this is doubtful, according to Griffiths,[3] who measures thermal conductivity by heating one surface of the material to be tested by placing it in contact with molten tin. R. A. Hornung [4] uses a hollow copper plate 20 inches by 20 inches by 1 inch (through which water flows backwards and forwards, entering and leaving at diagonally opposite corners) bedded upon a 2-inch layer of loose kieselguhr and covered with a layer of the material to be tested, upon which rests three coils of resistance wire, which is heated electrically. The coils are covered by another sample and a second plate identical with the lower one, the whole apparatus being packed loosely with kieselguhr into a box. The temperature of the cold side of the slab is the average of four readings of the temperatures of water entering and leaving the plates, whilst the temperature of the hot side is indicated by a thermo-couple placed between the two plates. The average amperage of the centre coil is the total amperage divided by 3, as the three coils are in parallel and the voltage is measured across the central third of the middle coil. The heat transmitted in B.T.U. per inch thickness may be calculated from the formula :

$$\frac{\text{voltage} \times \text{amperage} \times 3{\cdot}416 \times 24 \times \text{thickness in inches}}{\text{area in square feet} \times \text{diffusion temperature in } ^\circ \text{F.}}$$

R. A. Hornung also measures the thermal conductivity by a hot-air method in which the samples to be tested are made into a cubical box of 3 to 4 feet side, in which is placed a heating coil and fan to cause the circulation of the air. The coil is heated

[1] *Ber. Ver. Deut. Fab. Feuerfester Produkte*, **34**, 92 (1914).
[2] *Loc. cit.*, p. 516.
[3] *Trans. Faraday Soc.*, **12**, 193 (1916–17).
[4] *Trans. Amer. Cer. Soc.*, **18**, 192 (1916).

to the desired temperature, which is maintained for 48 hours to ensure uniform heating, and the temperatures of the interior and exterior are then taken every 10 minutes for 2–3 hours, the average being calculated and the transmission of heat per 24 hours in B.T.U. per square foot calculated from the formula :

$$\frac{(\mathrm{FA} \times \mathrm{FV}) + (\mathrm{CA} \times \mathrm{CV})\ 3{\cdot}416 \times 24}{\mathrm{D} \times \mathrm{A}},$$

where FA and CA are the amperages, and FV and CV are the voltages of the fan and coil respectively ; D is the difference in temperature, and A is the mean area in square feet.

For temperatures above 300° F., a heating coil may be used in a cylinder 8 to 10 inches diameter and 24 inches long, no fan being employed.

In A. T. Green's [1] determinations of the thermal conductivity the samples were heated through a hot plate by means of a graphite resistance furnace. The temperature was measured at three places : (*a*) on the hot face of the samples, (*b*) at a distance of 4 cm., and (*c*) at a distance of 5·4 cm. The thermal conductivity was then calculated from the formula :

$$\theta = \theta_0\left(1 - \frac{2}{\sqrt{\pi}}\int^{\frac{x}{2\sqrt{kt}}} e^{-\mathrm{B}^2} d\mathrm{B}\right),$$

where

$$\mathrm{B} = \frac{x}{2\sqrt{kt}} \quad \text{or} \quad \frac{\theta_0 - \theta}{\theta_0} = \frac{2}{\sqrt{\pi}}\int^{\frac{x}{2\sqrt{kt}}} e^{\mathrm{B}^2} d\mathrm{B},$$

where θ_0 is the temperature of the hot face, x is the distance, t is the time, θ is the temperature after the time t at the distance x, and k is the diffusivity.

The *Diffusivity* is the rise in temperature produced in 1 c.c. of the substance by 1 calorie acting during 1 second through 1 square cm. of a layer 1 cm. thick, having a temperature difference of 1° C. between its faces.

The coefficient of diffusion is represented by :

$$\frac{\mathrm{K}}{\overline{dh}},$$

where K is the amount of heat in gm.-cals. which is transmitted in 1 second through a plate 1 cm. thick per square cm. of its surface when the difference in temperature between the two sides is 1° C., d is the specific gravity, and h the specific heat of the material.

Fourier's law for the linear flow of heat is :

$$\frac{d^2\theta}{dx^2} = k\frac{d\theta}{dt},$$

where θ denotes temperature, x the distance from a hot surface, t the time, and k the

[1] *Loc. cit.*, p. 515.

diffusivity. Calculations based on this formula, made by Heyn, Bauer, and Wetzel, give much lower results for conductivity than those obtained by means of calorimeters.

The loss of heat through a furnace wall is given by the expression :

$$H = K(T_1 - T_0)\frac{S}{l},$$

where H represents the flow of heat, T_0 the temperature of the cold or outer surface, T_1 that of the hot or inner surface of the wall, S the area, l the thickness, and K the mean thermal conductivity between the temperatures T_0 and T_1.

If s is the inner area of the wall and S the outer area, the geometric mean is $\sqrt{sS}$ and

$$H = k(T_1 - T_0)\frac{\sqrt{sS}}{l}.$$

In electrical furnaces the term *thermal mho* is generally used to express in watts the heat radiated in gm.-cals. per second per cm. cube for a difference of 1° C., a watt being equivalent to 0·2388 calories per second. The reciprocal value of this, the *thermal ohm*, represents the difference of temperature divided by the flow of heat in watts per cm. cube.

The thermal conductivity expressed in C.G.S. units may be converted into thermal ohms by multiplying the reciprocal of the conductivity by 0·2388. To reduce gm.-cals. to watts, the reciprocal of the conductivity is multiplied by 4·186. The watts may be resolved into power as follows :—

Watts × 0·00134111 = horse-power.
Watts × 0·0568776 = B.T.U. per minute.
Watts × 0·0143329 = calories per minute.

Contact conductivity, or rather its reciprocal, contact resistance, which is denoted by R, represents the difference in temperature in ° C. between the hot body and the surrounding medium, divided by the number of watts or gram-calories per second which flows from each square cm. of surface.

$$\mathrm{R} = \frac{36{,}000}{2 + \sqrt{v}},$$

when v denotes the velocity of air (which results from the temperature difference) in cm. per second, and the loss of heat per square cm. surface per second for a difference in temperature of t° C. will be

$$\frac{t}{\mathrm{R}} \text{ cal. per second.}$$

The thermal conductivity is a very important property in ceramic materials. Thus, the walls of a furnace which is internally heated are required to have a low thermal conductivity so that as little heat as possible will be lost through them. The walls of a muffle, retort, or similar appliance, on the contrary, must have a high thermal conductivity in order that the heat may pass through them in order to heat

their contents. The application of the thermal conductivity of ceramic materials is further dealt with in Chapter XIII.

(*b*) **Convection,** in which the heated particles move away from the hotter to the cooler parts of the mass and carry " heat " with them. Convection can only occur in fluids, as the particles in a solid are not sufficiently mobile.

(*c*) **Radiation,** in which the heat is carried neither by conduction nor convection, but in a manner comparable to the transmission of light. Heat may be radiated instantaneously through space as well as through air and other gases, and when so radiated it scarcely affects the temperature of the medium through which the " rays of heat " are passed. There is a very close relationship between radiated heat and light. Both can be reflected by mirrors and deflected or refracted by prisms and lenses ; in fact, the chief difference between them appears to lie in the difference in wave length.

Hence, when a body is sufficiently heated, the heat-rays emit a form of light and the body is said to be " incandescent." When heat-rays are absorbed by any substance the latter is heated and its temperature increased in proportion to the amount of heat absorbed, but the air through which the heat-rays pass may remain at a much lower temperature. This is due to the fact that radiated heat is absorbed more by some surfaces than others, the nature of the surface being of greater importance, in this respect, than the composition of the heat-absorbing material. Similarly, the amount of heat radiated from a body varies according to the colour and nature of the radiating surface, being low for polished metal and high for rough black surfaces. In the latter, it is proportional to the fourth power of the absolute temperature—

$$E = k(T_1^4 - T_0^4),$$

where E denotes the radiation from a body at T_1 to one at T_0 and k is a constant. The radiation loss, apart from convection, is usually (for a temperature difference of 100° C.) 0·015 gram-cal. per second for each cm. of heat-radiating surface.

The General Effect of Heat on Substances [1]

Heat effects various changes upon any body subject to its influence, the principal ones being :

(*a*) A change in the temperature of the mass.
(*b*) A change in the volume of the material (expansion and contraction).
(*c*) A change in the physical state of the material.
(*d*) A change in other physical properties of the material.
(*e*) A change in the chemical composition of the mass.
(*f*) A change in the electrical condition of the mass.
(*g*) A change in the optical properties of the mass.

Changes in temperature may be purely physical in character and a simple result of what is termed the absorption of heat (this may simultaneously effect a change in

[1] The effects of heat on ceramic materials as distinct from other substances are considered in Chapter XIII.

the physical state of the substance, p. 523), or they may be the result of chemical changes which evolve or absorb heat.

Exothermal and Endothermal Changes.—The absorption of heat by a substance causes a change of state first by sensible heat which raises its temperature to a certain point and then by additional heat which becomes latent and effects the change of state from solid to liquid or from liquid to gas. By reconverting the changed substance into its original state the heat previously rendered latent is evolved as sensible heat and most of it can be recovered. When heat is absorbed and rendered latent by a change in the state of a substance, that change is termed *endothermal.* When the reverse change occurs and the latent heat is evolved, the change is termed *exothermal.* Neutralisation of acids by bases or alkalies is an exothermal reaction, but hydrolysis is an endothermal reaction. Thus, the neutralisation of caustic potash by hydrochloric acid is accompanied by the liberation of energy equivalent to 57·3 J or 136,947 calories, which may be expressed thus :

$$KOH + HCl = KCl + H_2O + 57{\cdot}3\ J.$$

Some endothermal reactions become exothermal at higher temperatures and *vice versa.* Consequently, a compound may be unstable at a low temperature, stable at higher temperatures and conversely.

The reversal of the direction of a reaction with a change of temperature shows how necessary it is to ascertain the conditions of a reaction when investigating the character of the change.

A compound formed with the evolution of heat requires the addition of more heat to decompose it (see also *Changes in Chemical Composition*, p. 528).

Changes in volume effected by heat result in either an increase or a decrease in the volume of the substance ; the former is termed *expansion* and the latter *contraction* or *shrinkage.* These changes are often of great technical importance, especially when substances which undergo such changes are made into articles which are required to be of definite size within very narrow limits. Thus, first-class firebricks are not expected to vary in length by more than 1 per cent., whilst for some electrical fittings made of stoneware or porcelain a much greater degree of accuracy in size is required.

The changes in volume caused by the action of heat may be divided into two groups : (*a*) reversible, and (*b*) irreversible changes.

(*a*) *Reversible volume-changes* are those in which the volume of a substance changes on the application of heat, but the original volume is regained when the heat is withdrawn, *i.e.* when the substance is cooled to the original temperature. Such changes are usually of a wholly physical nature.

(*b*) *Irreversible changes* are those in which any increase or decrease in volume which may occur is not reversed on cooling. Such a change may be the result of the formation of a substance of different specific gravity, such as the conversion of quartz to cristobalite, or some change of a chemical character whereby new compounds are formed. The conversion of a substance into another allotropic form is usually classed as a physical change, but it is also chemical in character, as when the chemical

constitution of the substance is examined it will be found to be different with each allotropic form. When a chemical change occurs a change in volume is almost inevitable, though, for various reasons, it is not always easy to recognise.

The term " irreversible " is not strictly correct, as theoretically all changes are reversible under suitable conditions. This term, therefore, should be understood in a comparative sense as a change which is so extremely slow that it may be considered under ordinary conditions to be irreversible as distinct from the more readily reversible changes which occur at an appreciable speed.

The unit of measurement of the reversible change in volume on heating or cooling is termed the *coefficient of expansion* or *contraction* ; it is expressed as a fraction of the length, cross-sectional area, or volume of the substance (the latter being taken as unity) when heated so that its temperature rises 1° C., though any suitable temperature may be used, provided it is specified. The coefficient of expansion may be expressed in terms of length, *i.e.* the coefficient of linear expansion, or in terms of volume, *i.e.* the coefficient of cubical expansion. If the coefficient of linear expansion is represented by a, the original length of the piece being l_o at 0° C. and l_t at t° C., then

$$l_t = l_o(1 + at).$$

Hence, if the length prior to expansion be unity, that after expansion will be $(1+a)$ and the volume after expansion will be $(1+a)^3$ or $1+3a+3a^2+a^3$. As a is a small fraction, a^2 and a^3 will often be so small as to be negligible, and it is then sufficient to regard the volume of the expanded material as $(1+3a)$. Hence, the coefficient of cubic expansion is almost exactly three times the linear coefficient. If the linear expansion or contraction is as high as 10 per cent., omitting the fractions as suggested will produce an error of about 10 per cent. of the total linear contraction.

Most pure substances expand suddenly when melted, but a few (notably ice and bismuth) contract. Thus, 1000 c.c. of ice yield only 910 c.c. of water at 0° C. This expansion or contraction relates to the individual particles and not to the mass as a whole, as in a porous material the air-spaces may be filled by the molten material.

The expansion of materials on heating may be determined in various ways. Where it is large, as in the case of some metals, a bar is heated with one end fixed and the other in contact with an indicating lever and the amount of deflection noted. The chief difficulty lies in avoiding or neutralising the expansion of the furnace in which the test-piece is heated.

P. A. Boeck [1] endeavoured to eliminate this error by heating a cylindrical test-piece in an electric tube furnace, closed at one end and supported upon two brass pillars, the tube being fastened securely to the support opposite the closed end, but allowed to slide freely on the other support. By this means the tube of the furnace can only expand in one direction. The test-piece is placed between two smaller quartz tubes into the main tube of the furnace and is supported to prevent contact with the walls of the tube by platinum rings. As the end of the main tube is closed, the test-piece and the inner quartz tubes are only able to expand in a direction opposite to that of

[1] *Trans. Amer. Cer. Soc.*, **14**, 470 (1912).

the main tube, so that the expansion of the inner quartz tubes neutralises that of the outer tube; any residual change in volume is due entirely to the test-piece. The expansion of the test-piece is measured by means of a cross-hair fitted on to the inner tube at the open end of the furnace and viewed through a microscope having a micrometer scale. The temperature of the test-piece is measured at the same time by means of a thermo-couple.

Hodsman and Cobb [1] use a similar method, but they arranged so that the outer tube and the distance-pieces both expanded in the same direction and both had fiduciary marks on them, so that their relative positions at different temperatures could be measured, the movement being due to the expansion or contraction of the test-piece as the two pieces of silica were assumed to expand equally.

Mellor uses a much simpler direct method, by having two fiduciary marks (such as fine saw cuts in which fine platinum wires are fixed) and measuring their distance apart by two cathetometers placed outside the furnace in which the test-piece is heated.

The permanent volume changes in ceramic materials may readily be measured by determining the length or cubical contents of the test-piece before and after treatment.

The provisional standard specification of the English Ceramic Society [2] for testing the contraction of clay consists in drying the clay at a temperature not exceeding 70° C., crushing it so that it will pass through a 28-mesh sieve, mixing it with water and shaping it into a suitable form, by means of a mould. The test-piece is marked with vertical lines 9 cm. apart and allowed to dry, first at the ordinary temperature, then for four to five hours at 70°–80° C., and finally at 110° C. The drying shrinkage is then measured. The test-piece is then heated in a furnace at the rate of not more than 100° C. per hour to 900° C., and afterwards at the rate of not more than 4 cones (about 80° C.) per hour to the end of the firing. The test-piece is then allowed to cool and is measured. The difference between the vertical lines (*a*) before and after drying gives the drying shrinkage, (*b*) after firing and after drying gives the kiln shrinkage, and (*c*) before drying and after firing gives the total shrinkage. These results are usually expressed as a percentage of the distance between the fiduciary marks before drying the test-piece. The after-expansion or after-contraction of refractory materials should be determined, according to the provisional specification of the English Ceramic Society,[2] by means of a test-piece 3 inches long and 1–2 inches wide and deep, the opposite ends being ground parallel on an abrasive wheel. The test-piece is fired to Cone 14, if it contains less than 80 per cent. silica or Cone 12 if it contains more than 80 per cent., maintained at the correct temperature for two hours and then cooled, the size before and after heating being accurately measured.

The American Ceramic Society [3] suggest the use of test-pieces $1\frac{1}{8} \times 1\frac{1}{8} \times 1\frac{7}{8}$ inch for shrinkage tests.

[1] *J. Soc. Glass Tech.*, **3**, 201 (1919).
[2] *Trans. Eng. Cer. Soc.*, **17**, 300 (1918).
[3] *J. Amer. Cer. Soc. Year Book*, 1921–22, II, 39.

When the shrinkage by volume is to be determined, a volumeter such as is used for porosity determinations (p. 84) must be used, the volume of the sample being determined before and after the test and the percentage of volume change calculated from these figures.

It is sometimes desired to determine the number of times a sample can be quickly heated and cooled, before it cracks. This is termed its *resistance to spalling* and is found by weighing the test-pieces and heating them to a temperature of 1350° C. for one hour until the temperature of the test-pieces is uniform throughout. Each test-piece is exposed for fifteen minutes to a blast of cold air from a $\frac{3}{4}$-inch nozzle, supplied with air at the rate of 27 cubic feet per minute. The test is repeated ten times and the bricks are then allowed to cool and are reweighed. The loss in weight expressed as a percentage of the original weight is regarded as due to spalling.

A tentative specification of a test of resistance to spalling issued by the American Society for Testing Materials [1] consists in heating the brick to 1400° C. for five hours, exposing one end in the furnace to 1350° C. for one hour, then removing and placing in cold running water for three minutes. The treatment is repeated until the end of the brick spalls off, the number of treatments required being regarded as a measure of the resistance of the article to spalling.

Changes of Physical State.—When sufficient heat is applied to a solid substance it will, in time, cause the solid to change to a liquid and finally to a gas, though in some cases the heat required to effect these changes is so great that they are almost unattainable. When a substance is placed in a furnace, the temperature of which rises at a uniform rate, the temperature of the substance will also rise uniformly until a point is reached at which either a change in state or decomposition occurs. In the former case, the substance will commence to liquefy, *i.e.* to turn into the liquid state. During this change, or liquefaction, the temperature of the substance will remain constant, and if the substance is pure the temperature will remain constant until liquefaction is complete. When the substance is entirely liquid the temperature again commences to rise. If the substance can be converted into gas without decomposition, its temperature will continue to rise on prolonged heating until the gasification or volatilisation of the substance occurs, when the rise in temperature will again cease until all the liquid has been converted into gas. After this, the temperature will rise indefinitely. The temperature at which the arrest, due to liquefaction, takes place is termed the *melting-point*; that at which the arrest due to vaporisation occurs is termed the *boiling-point*. Thus, water remains at 0° C. until wholly converted into ice and at 100° C. until wholly converted into steam.

The heat absorbed by any material without the latter showing any rise in temperature is said to be rendered latent or inactive and is termed *latent heat*, in order to distinguish it from the "sensible heat" which causes an immediate rise in temperature. Probably the best conception of latent heat is that which regards it as the power required to overcome the mutual attraction of the molecules and by separating them converts the substance first into a liquid and afterwards into a gas. Hence, the *latent heat of fusion* is the amount of heat required to convert unit weight

[1] *Tent. Stand.*, 297 (1922).

of a solid at the temperature at which fusion can occur wholly into a liquid. It may be determined in the same manner as the specific heat (p. 512), by means of a calorimeter into which a weighed quantity of the molten material is placed. The heat evolved is determined and from it is subtracted the amount of heat evolved by treating an equal weight of the same substance in the solid state at the same temperature in a precisely similar manner ; the difference is the latent heat of fusion.

The latent heat of fusion may be roughly estimated by a consideration of the heating and cooling curves of the material together with the heat capacity of the crystalline and the liquid material near its melting-point, but this method is only accurate to within about 15 per cent.

Similarly, the *latent heat of vaporisation or of gasification* is that which is required to convert a liquid, previously heated to its boiling-point, wholly into vapour or gas. The absorption of this heat does not cause any rise in the temperature of the liquid, but is used (*a*) to overcome the forces of attraction between the molecules of liquid, and (*b*) to push back a suitable volume of air to make room for the liberated vapour. In a vacuum (*b*) does not enter into the problem, and consequently, less heat is required to vaporise or evaporate a liquid so that its boiling-point is correspondingly reduced.

The quantity of heat required to produce the molecular weight (in grams) of vapour formed from a liquid is termed the *molecular heat of vaporisation* or the *molal latent heat* ; it varies with the boiling-point of the liquid. According to Trouton, the molal heat of vaporisation of a liquid at atmospheric pressure in calories $= 20{\cdot}3 \times$ the boiling-point on the absolute scale. As the pressure increases, the latent heat decreases until at the critical pressure no heat is required.

The *melting-point* of a substance is the lowest temperature at which the complete conversion from the solid to the liquid state can occur.

Although it is sufficient, for most purposes, to regard the melting-point of a substance as the lowest temperature at which it becomes fluid, the conditions under which refractory materials melt are so complex that this definition does not apply.

A much better definition is that which regards the melting-point as the temperature at which the crystalline and amorphous states of the substances are in equilibrium, and this temperature is not affected by adding a small amount of heat to or withdrawing it from the material. In accordance with this definition, the melting-point of a substance may be identified in three different ways :—

(i) By a change in state, from solid to liquid.

(ii) By a change in structure, from crystalline to amorphous.

(iii) By a change in energy, due to absorption or liberation of heat as shown by a time-temperature graph (p. 464).

If the substance is a single, pure element or a compound which does not decompose on fusion, the melting-point will be sharply defined as the point at which a rise in temperature ceases until the substance has been completely liquefied. In the presence of impurities, or when a mixture instead of a single substance is heated, fusion takes place gradually over a range of temperature and the material softens and may lose its shape at a temperature much below that at which it can be completely

fused. Some single compounds which have a very low thermal conductivity, such as silica, do not show a sharply defined melting-point, but melt gradually over a range of about 110° C. Thus, whilst the true melting-point of silica, according to Day and Shepherd, is about 1600° C., its viscosity is so great that it does not flow or change its shape until a temperature of about 1750° C. is reached. Such substances also show a curious difference in melting-point according to the size of the particles and the rate at which the temperature rises. As their conductivity is so low, an impractical length of time would be required to fuse a quantity completely at the same temperature as a few grains can be fused, and consequently, bricks and other articles made of such materials may sometimes be fused at temperatures which are actually above their true melting-point if the duration of the heating is not too long.

In consequence of the great time required to effect complete fusion at the true melting-point, this point is seldom determined. The so-called "fusion-point" of a ceramic material usually refers to the lowest temperature at which any appreciable signs of fusion are visible, such as the rounding of the sharp edges of the test-piece.

For many purposes, the temperature at which a test-piece the shape of a Seger cone (fig. 50) loses its shape by bending—termed the softening-point—is substituted for the melting-point in determining the fusibility or, conversely, the refractoriness [1] (see p. 526). There is, however, no direct relationship between the softening-point and the true melting-point of a ceramic material. At the same time—assuming the true melting-point to be indeterminable—the softening-point, which is higher, serves at least as an indication of a temperature at which an appreciable change of state occurs.

The apparent melting- or softening-point of a substance depends upon :—

(*a*) The chemical composition of the material.
(*b*) The amount and nature of any impurities present.
(*c*) The pressure applied.
(*d*) The rate at which the temperature of the furnace rises.
(*e*) The thermal conductivity of the material.
(*f*) The shape and size of the piece to be heated.

The chemical composition of the material is an inherent property and the only alteration in the conditions of heating which can affect it is the nature of the atmosphere in the furnace. If the material contains reducible compounds, such as ferric oxide, and the material is heated in a reducing atmosphere, the formation of ferrous silicate and other "reduced" compounds may seriously affect the melting-point. For this reason, in determining the softening-point or melting-point of a ceramic material the heating should always be under oxidising conditions. Raoult discovered in 1882 that when any substance dissolves in another (molten) substance the melting-point of the latter is reduced in proportion to the amount of material dissolved. If the

[1] If the term "refractoriness" is understood to include resistance to furnace conditions, the attack of slags, gas, etc., the abrasive action of flue dust and similar deteriorating influences, it becomes almost impossible to define it, so that its use should be confined to the resistance of a material to heat under oxidising conditions in a "clean" atmosphere.

added substances are in proportion to their molecular weights, they will reduce the melting-point of the "solvent" by the same amount, *i.e.* equimolecular solutions in a given solvent have the same melting-point. Ludwig has made use of this fact in calculating the refractoriness of fireclays from their composition (p. 382).

If a substance contracts on melting, its melting-point will be reduced by the application of external pressure, and as ceramic materials occupy less space when molten than in the solid state, if pressure is applied to any ceramic article or test-piece, it will reduce its melting-point. In addition, the softening-point will be reduced because the pressure enables the particles to move readily and thereby show distortion when a much smaller percentage of molten material is present than would be the case if no pressure were applied. The application of pressure does not affect the true melting-point of the material; it merely indicates at an earlier stage than would otherwise be noticeable the extent of liquefaction which has occurred.

The rate at which the temperature of the furnace rises affects the apparent softening-point or melting-point merely as a result of the thermal conductivity of the material. Where the conductivity is low the heat penetrates the material slowly, and if the external temperature is rising rapidly the temperature at which an appreciable amount of fusion occurs is higher than would be required if the temperature were rising more slowly. Thus, Cone 5 has a nominal fusing-point of 1180° C., but it will fuse at 1130° C. if kept at this temperature for 24 hours, and at 1100° C. if heated for five days at that temperature.

If only a very small quantity of material—say a few grains—is heated, the heat penetrates these separate particles much more readily than a larger mass. Consequently, the separate particles will melt at a lower temperature than the larger mass, although both samples are composed of the same material.

Add to these considerations the fact that most ceramic materials contain variable amounts of impurities which, by forming solid solutions and in other ways, reduce the melting-point of the chief constituent and it is easy to understand that such materials do not exhibit a sharply defined melting-point, but show signs of fusion over a relatively long range of temperature before the fusion is complete.

In comparing the melting- or softening-points of different materials, one of the most serious sources of error lies in heating the furnace too rapidly or at different rates for different samples. Thus, if a fireclay has a softening-point corresponding to Cone 28 when heated slowly, it may easily be made to appear to have a softening-point equal to Cone 32 or even higher if it is heated very rapidly. This serious difference is wholly due to the low thermal conductivity of the material which makes it necessary to heat the furnace slowly when making tests of this nature. A rise of 10° C. per minute is usually satisfactory and is widely accepted as a standard rate of heating.

Two methods are available for the *determination of the melting- or softening-points* of ceramic materials:

(*a*) The sample is heated at a definite rate (usually 10° C. per minute) in a suitable furnace, under oxidising conditions, and the temperature of the sample is measured at frequent intervals or continuously by means of a thermometer or pyrometer,

and the temperature at which fusion occurs is noted. This method is quite satisfactory for pure substances with a high thermal conductivity, because such substances show a marked arrest in the rising temperature of the sample during the fusion. This method may also be used for determining the fusion-point of individual particles, as their change of shape when fusing can be observed under the microscope.

In a modification of this method, the sample is heated to a definite temperature, withdrawn from the furnace and examined; if no signs of fusion are observable, another sample of the same material is heated to a still higher temperature prior to examination. By this means, the point at which " first signs of fusion " occur can be ascertained after a number of trials.

In order that the results may be comparable, the size and shape of the test-piece and the rate of heating must be the same in each case.

(*b*) With substances having a low thermal conductivity, it is often more convenient to determine the softening-point by heating it in the manner just described with similar-sized pieces of other (standard) materials also of low thermal conductivity, the softening-points of which have been accurately determined. That of the standard material which behaves like the sample is taken as the temperature corresponding to the softening-point of the latter. The shape of test-piece and standards most generally favoured is that of the Seger cones (p. 540), the sample being cut or finely powdered, mixed with a little dextrin if necessary, and moulded to the desired shape, dried, and placed with suitable Seger cones in an electric, gas-blast, or Deville furnace, and heated at a suitable rate (about 10° C. per minute). Seger recommended that the critical point (softening-point) should be taken as that at which the apex of the cone or sample bends over and just touches the base upon which it stands, but some other investigators prefer to withdraw the sample from the furnace and examine it for " the first signs of fusion " as indicated by a rounding of its edges. This method is the one specified by the Institution of Gas Engineers in its Standard Specification.

It is, of course, necessary that the temperature should be uniform throughout the furnace; otherwise, some of the cones will be at different temperatures from the test-piece. They should, therefore, be placed as close together as possible, and it is often convenient to cover them over with an inverted crucible so as to protect them from currents and eddies and ensure a more uniform heating.

Kanolt [1] determines the melting-point of refractory materials by placing the sample on a bed of alundum in the bottom of a refractory tube, approximating to the composition $Al_2O_3SiO_2$ (sillimanite) in the case of materials melting below 1800° C. For higher temperatures, graphite crucibles are used. Observations are made through a window in the top of the furnace.

In determining the melting- or fusion-point of a substance, it is important to use a container which will not contaminate the material being tested. Magnesia may be conveniently heated in graphite crucibles, but oxides which form carbides or are reduced to the metallic state should preferably be heated in a bauxite or tungsten container.

If the material to be tested is liable to shrink or crack during the heating, it is often

[1] *Trans. Amer. Cer. Soc.*, **15**, 167 (1913).

convenient to make the test-piece partly with calcined material, as this lessens the contraction and liability to cracking without altering its refractoriness.

The *boiling-point* of a substance is the temperature at which it is converted into vapour at such a rate that its vapour pressure is that of a column of mercury 760 mm. in length or 1 atmosphere. Most ceramic materials have boiling-points which are so high as to be outside the range of attainable temperatures, so that their boiling-points are not of great importance. The chief exception to this is water which, when pure, has a boiling-point of 100° C. or 212° F. The boiling-point of any substance is reduced if the pressure of the atmosphere in which it is reduced is also reduced, so that water can be boiled rapidly *in vacuo* at about 60° C., and slowly at lower temperatures.

If a liquid is heated above its boiling-point in a closed vessel so that the vapour of the liquid cannot escape, the vapour-pressure will increase in proportion to the heat absorbed. A typical example of this is the pressure of steam in an ordinary boiler. Water heated under pressure has a more solvent action than that at the ordinary boiling-point, and is probably one cause of the decomposition of felspar and other minerals from which clay is derived. Any substances which dissolve in a liquid will increase the boiling-point of the latter in proportion to the concentration of the solution.

Changes in other physical properties which are effected by heat include:

(i) Changes in specific gravity (Chapter V).
(ii) Changes in porosity (Chapter II).
(iii) Changes in hardness (Chapter III).
(iv) Changes in strength, including those in toughness, elasticity, etc. (Chapter IV).
(v) Changes in crystalline form (Chapter I).
(vi) Changes in texture (Chapter I).
(vii) Changes in viscosity (Chapter XI).

These various changes are also dealt with in the next chapter.

Changes in Chemical Composition.—Heat is an important factor in chemical reactions as it facilitates such changes as decomposition, oxidation, reduction, etc. Indeed, most chemical changes take place much more rapidly at a high temperature than at a lower one. In some cases, the velocity of a reaction is doubled if the temperature of the reacting substances is raised a few degrees. When a reaction occurs slowly it may usually be completed far more quickly by the aid of heat.

Some substances evolve heat at the moment of crystallisation, plaster of Paris and Portland cement being good examples. When either substance is mixed with water to form a paste, the temperature rapidly rises, the mass " sets " solid, and if examined later will be found to have crystallised.

Quicklime combines with water, forming calcium hydroxide, and also evolves heat during the process.

In the former case, the heat is termed *heat of crystallisation*, in the latter, *heat of combination*. Conversely, most substances containing water of crystallisation or

" combined water " (p. 337) part with it when heated. The effect of heat in producing endothermal and exothermal physical changes has been described on p. 520. The same terms are applied when heat is absorbed or evolved as the result of chemical reactions. The chemical changes accompanied by heat-phenomena may be investigated quantitatively and the heats of reaction may be accurately determined. The principal groups of reactions accompanied by a change in temperature may be grouped according to the—

(*a*) heat of solution ;
(*b*) heat of combination (including that of neutralisation and combustion) ;
(*c*) heat of dissociation.

The *heat of solution* of a substance appears to be due to a combination of the substance and the solvent and to depend upon (i) the nature of the substance and solvent, and (ii) the concentration. The greater the concentration, the more rapidly is heat evolved. Thus, the addition of 1 mole of HCl to 250 c.c. of water evolves 16,950 calories. The effect of the addition of further quantities of water is as shown in Table CXXXVI, due to E. B. Millard :—

TABLE CXXXVI.—*Heat of Solution of Hydrochloric Acid*

Amount of Water added, c.c.	Total Volume, c.c.	Calories Evolved.	Total Calories Evolved per Mole of Acid.
250	500	450	16,950
500	1000	350	17,250
1000	2000	150	17,400

The great amount of heat evolved when sulphuric acid is dissolved in water is well known. A corresponding amount of heat is evolved when many other substances are dissolved, *e.g.* phosphoric pentoxide, anhydrous copper sulphate, metallic sodium, lime, etc. Conversely, the solution of saltpetre, or ammonium nitrate in water or of common salt in ice, is accompanied by a reduction in the temperature of the mixture.

On slaking quicklime,

$$CaO+H_2O=Ca(OH)_2,$$

15 Calories are evolved, whilst if the hydrate is dissolved in water, 3 more Calories are liberated per mole of the hydrate.

The nature of the reactions between the solute and solvent in " simple " solution is not completely understood, though it seems fairly clear that some form of combination must occur.

Heat of Combination.—When two solutions capable of reacting with each other are

mixed, the heat-changes which occur are dependent on (*a*) the extent of the ionisation of the dissolved substances, and (*b*) whether the products of the reaction are soluble or insoluble in the fluid. Solutions which are highly ionised and produce soluble compounds usually have very low heats of reaction, but if a precipitate is formed the heat-effect may be considerable. The neutralisation of an acid by a base when both are in solution is a type of exothermal reaction whose thermal properties are easily investigated, but a similar investigation of the reactions of ceramic materials is much more difficult on account of their insoluble character.

The heat of neutralisation between an ionised acid and ionised base is about 13,800 calories per molecule of water formed. The effect is very different between slightly ionised solutions, because the heat effect is due to the following reaction :—

$$H^+ + OH^- = H_2O + 13{,}800 \text{ calories at } 20^\circ \text{ C.}$$

This value is increased at lower temperatures and decreased at higher ones.

In more general terms, the heat of reaction, *i.e.* the amount of heat absorbed or evolved during a chemical reaction at any temperature, is expressed by the formula :

$$Q_2 = Q_1 - \triangle Cp(T_2 - T_1),$$

where Q_2 is the quantity of heat in the system at the higher temperature, Q_1 is that at the lower temperature, $\triangle Cp$ is the increase in heat capacity of the system during the reaction, and T_2 and T_1 are the higher and lower temperatures respectively.

According to Berthelot's law, " every reaction which takes place independently of the addition of energy from outside the system tends to form the combination which is accompanied by the greatest evolution of heat." Hence, when carbon burns, CO_2 is formed in preference to CO. The final product in any reaction may usually be predicted by means of this law.

Thermo-chemical changes and reactions may be expressed by ordinary chemical equations to which are added the thermal effects noted. Thus,

$$\underset{\text{solid.}}{CaCO_3} = \underset{\text{solid.}}{CaO} + \underset{\text{gas.}}{CO_2} + 175\text{J (or 41,825 calories).}$$

This equation represents an absorption of heat which is necessary to decompose the calcium carbonate.

$$C + O_2 = CO_2 + 394 \text{ J (or 94,166 cals.)}$$
$$C + O = CO + 284 \text{ J (or 67,876 cals.)}$$
$$CO + O = CO_2 + 110 \text{ J (or 26,290 cals.)}$$

If the heats of formation of two compounds are known, the net effect of a reaction may be calculated. Thus, the heat of formation of magnesium chloride is 632 J, that of the sodium chloride is 408 J, whence, in the reaction

$$MgCl_2 + Na_2 = 2NaCl + Mg$$
$$-632 + 2 \times 0 = 2 \times -408 + 0 + x$$
$$x = 184 \text{ J.}$$

The reaction is, therefore, exothermic, the heat equivalent to 184 J or 44,000 calories being liberated.

According to Hess's law, the quantity of heat evolved or absorbed by a reaction which takes place in two or more stages is the same as would have been evolved or absorbed if the reaction had occurred in one stage. Thus, the formation of carbon monoxide from carbon and oxygen is accompanied by the evolution of 67,876 calories, the formation of carbon dioxide from carbon monoxide by the evolution of 26,290 calories, and in the formation of carbon dioxide from carbon the same amount of heat (viz. 94,166 calories) is evolved as if the formation had taken place in the two stages just mentioned. Hence—

(i) The heat of formation of a compound is independent of its mode of formation.

(ii) The thermal value of a reaction is independent of the time occupied by the process.

(iii) The thermal value of a reaction is the sum of the heats of formation of the final products of the reaction less the heats of formation of the initial products of the reaction.

The heat of formation of various oxides from their elements is shown in Table CXXXVII.

TABLE CXXXVII.—*Heat of Formation*

Oxides.	Calories.	Oxides.	Calories.
H_2O	58,060	Na_2O	100,900
CO	29,000	K_2O	98,200
CO_2	97,000	FeO	65,700
SiO_2	196,000	Fe_2O_3	195,600
MgO	143,000	Fe_3O_4	270,800
BaO	133,400	$CaCO_3$	273,800
CaO	131,500	$MgCO_3$	269,900
Al_2O_3	392,600	$CaSO_4$	321,800

The *heat of dissociation* of a substance is the amount of heat evolved when the substance is dissociated into its constituents. It is the same as the amount of heat absorbed when the compound is produced by the union of its constituents. The amount of heat rendered latent when a compound forms or evolved when the compound is dissociated is often termed its heat-content. Thus, a compound which when formed absorbs x calories will have a heat-content of $+x$ calories, but if x calories are evolved when it is formed its heat-content will be $-x$ calories.

The heats of chemical reactions are often obscured by unobserved latent heats, by heat spent in doing work of different kinds, also by the dissipation of heat in the act of solution, by the effects of allotropism and isomerism, by a preliminary

dissociation of the reacting molecules and by differences in the specific heats of the initial and final products of the reaction.

From the foregoing it will be seen that the study of thermal changes which occur during the heating and cooling of substances is very important (p. 464) ; it is dealt with more fully on p. 599.

In dealing with complex materials, like those used in ceramics, an investigation of the various points at which endothermal and exothermal changes occur is often a valuable aid to an understanding of the changes which occur when such materials are heated either in the course of manufacture or in use. It reveals the nature of the substances formed under certain conditions of heating and cooling, and thereby greatly facilitates the control of the production of refractory and other ceramic materials in which certain properties are required to be constant within somewhat narrow limits.

Pouillet Effect.—In 1822, Pouillet showed that sand, alumina, glass, etc., become heated when wetted with water ; this is generally known as the Pouillet effect. The heat evolved is proportional to the mass of the powder and to the exposed area of the solid. The heat evolved at 7° C. is nearly 0·00105 cal. per sq. cm. Below 4° C. there is a cooling effect instead of a heating one.

Electrical Changes.—Heat may cause two kinds of electrical changes : (*a*) it may generate a current of electricity, and (*b*) it may increase the power of the substance for conducting electricity. Conversely, the generation and conduction of electricity produces heat. The generation of electricity as the result of heating ceramic materials is not of great significance, but the changes effected by heat in the electrical conductivity of such material is often very important, especially in the case of electrical insulating materials. The passage of a powerful electric current through an insulator generates heat, and as the electrical conductivity increases rapidly with an increase in temperature, the insulating properties rapidly diminish with an increase in the voltage of the applied current when once a passage of the current through the insulator has been established.

The electrical properties of ceramic materials are further dealt with in Chapter XIV.

Changes in Optical Properties.—Heat effects various changes in the optical properties of substances, these changes being usually a result of some change in the physical state of the substance. Thus, the change from one allotropic form of a substance to another will usually cause a change in the optical properties, and a change from the crystalline to the glassy or amorphous state will also effect a change in the optical properties of a substance.

The crystalline form and, in some cases, the colour may alter as a result of heating. For further information on the optical properties of ceramic materials see Chapter XV.

Temperature Measurement

In order to compare the temperature of various substances or that of the same substance at different times it is necessary to have a unit of temperature, which is

commonly termed a *degree*. Unfortunately, there are two entirely different units in common use, each kind being the basis of a different *scale*.

The *Fahrenheit* scale of temperature consists of 212°, the difference between the two points on a thermometer indicating the temperature of melting ice (32° F.) and that of boiling water (212° F.) being divided into 180 equal parts or degrees.

In the *Centigrade* or *Celsius* scale of temperature the position on the thermometer indicated by the melting-point of ice is taken as 0° and the boiling-point of water as 100°.

Consequently,

$$y^\circ \text{ C.} = (x^\circ \text{ F.} - 32)\frac{5}{9}$$

$$x^\circ \text{ F.} = \left(y^\circ \text{ C.} \times \frac{9}{5}\right) + 32.$$

The Centigrade scale is the one chiefly used for scientific work, but for some purposes the relation between the temperature and some of the other properties of a substance or the changes in the conditions to which it is subjected are more easily recognised if the *Absolute scale of temperature* is used. This is simply the Centigrade scale, modified so that its zero is −273° C., and 0° C.=273° A. At the zero-point on the Absolute scale all gases cease to exist as such, and various other phenomena occur which show that this temperature is a natural critical point. This scale is based on what is known as the Mariotte-Gay Lussac law :—

$$pv = p_0v_0(1 + \alpha t),$$

where p, v, and t are the pressure, volume, and temperature (in °C.) of a perfect gas, p_0 and v_0 being the corresponding pressure and volume at zero on the Absolute scale, and $\alpha = 1/273$. Hence,

$$pv = p_0v_0\left(1 + \frac{t}{273}\right)$$

and by substituting T (the temperature on the Absolute scale corresponding to t° C.) for $273+t$,

$$pv = \frac{p_0v_0}{273} \times \text{T}$$

whence the well-known equation,

$$pv = \text{RT}.$$

To convert any temperature on the Centigrade scale to °A., it is merely necessary to add 273 and *vice versa*, *i.e.*

$$x^\circ \text{ A.} = y^\circ \text{ C.} + 273$$
$$y^\circ \text{ C.} = x^\circ \text{ A.} - 273$$

Table CXXXVIII shows a comparison of the various temperature scales.

TABLE CXXXVIII.—*Centigrade and Fahrenheit Scales*

° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.
0	32·0	41	105·8	82	179·6	123	253·4	164	327·2
1	33·8	42	107·6	83	181·4	124	255·2	165	329·0
2	35·6	43	109·4	84	183·2	125	257·0	166	330·8
3	37·4	44	111·2	85	185·0	126	258·8	167	332·6
4	39·2	45	113·0	86	186·8	127	260·6	168	334·4
5	41·0	46	114·8	87	188·6	128	262·4	169	336·2
6	42·8	47	116·6	88	190·4	129	264·2	170	338·0
7	44·6	48	118·4	89	192·2	130	266·0	171	339·8
8	46·4	49	120·2	90	194·0	131	267·8	172	341·6
9	48·2	50	122·0	91	195·8	132	269·6	173	343·4
10	50·0	51	123·8	92	197·6	133	271·4	174	345·2
11	51·8	52	125·6	93	199·4	134	273·2	175	347·0
12	53·6	53	127·4	94	201·2	135	275·0	176	348·8
13	55·4	54	129·2	95	203·0	136	276·8	177	350·6
14	57·2	55	131·0	96	204·8	137	278·6	178	352·4
15	59·0	56	132·8	97	206·6	138	280·4	179	354·2
16	60·8	57	134·6	98	208·4	139	282·2	180	356·0
17	62·6	58	136·4	99	210·2	140	284·0	181	357·8
18	64·4	59	138·2	100	212·0	141	285·8	182	359·6
19	66·2	60	140·0	101	213·8	142	287·6	183	361·4
20	68·0	61	141·8	102	215·6	143	289·4	184	363·2
21	69·8	62	143·6	103	217·4	144	291·2	185	365·0
22	71·6	63	145·4	104	219·2	145	293·0	186	366·8
23	73·4	64	147·2	105	221·0	146	294·8	187	368·6
24	75·2	65	149·0	106	222·8	147	296·6	188	370·4
25	77·0	66	150·8	107	224·6	148	298·4	189	372·2
26	78·8	67	152·6	108	226·4	149	300·2	190	374·0
27	80·6	68	154·4	109	228·2	150	302·0	191	375·8
28	82·4	69	156·2	110	230·0	151	303·8	192	377·6
29	84·2	70	158·0	111	231·8	152	305·6	193	379·4
30	86·0	71	159·8	112	233·6	153	307·4	194	381·2
31	87·8	72	161·6	113	235·4	154	309·2	195	383·0
32	89·6	73	163·4	114	237·2	155	311·0	196	384·8
33	91·4	74	165·2	115	239·0	156	312·8	197	386·6
34	93·2	75	167·0	116	240·8	157	314·6	198	388·4
35	95·0	76	168·8	117	242·6	158	316·4	199	390·2
36	96·8	77	170·6	118	244·4	159	318·2	200	392·0
37	98·6	78	172·4	119	246·2	160	320·0	201	393·8
38	100·4	79	174·2	120	248·0	161	321·8	202	395·6
39	102·2	80	176·0	121	249·8	162	323·6	203	397·4
40	104·0	81	177·8	122	251·6	163	325·4	204	399·2

TABLE CXXXVIII—*Continued*

° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.
205	401·0	246	474·8	287	548·6	328	622·4	430	806
206	402·8	247	476·6	288	550·4	329	624·2	440	824
207	404·6	248	478·4	289	552·2	330	626·0	450	842
208	406·4	249	480·2	290	554·0	331	627·8	460	860
209	408·2	250	482·0	291	555·8	332	629·6	470	878
210	410·0	251	483·8	292	557·6	333	631·4	480	896
211	411·8	252	485·6	293	559·4	334	633·2	482	900
212	413·6	253	487·4	294	561·2	335	635·0	490	914
213	415·4	254	489·2	295	563·0	336	636·8	500	932
214	417·2	255	491·0	296	564·8	337	638·6	538	1000
215	419·0	256	492·8	297	566·6	338	640·4	593	1100
216	420·8	257	494·6	298	568·4	339	642·2	600	1112
217	422·6	258	496·4	299	570·2	340	644·0	649	1200
218	424·4	259	498·2	300	572·0	341	645·8	700	1292
219	426·2	260	500·0	301	573·8s	342	647·6	704	1300
220	428·0	261	501·8	302	575·6	343	649·4	760	1400
221	429·8	262	503·6	303	577·4	344	651·2	800	1472
222	431·6	263	505·4	304	579·2	345	653·0	815	1500
223	433·4	264	507·2	305	581·0	346	654·8	871	1600
224	435·2	265	509·0	306	582·8	347	656·6	900	1652
225	437·0	266	510·8	307	584·6	348	658·4	926	1700
226	438·8	267	512·6	308	586·4	349	660·2	982	1800
227	440·6	268	514·4	309	588·2	350	662·0	1000	1832
228	442·4	269	516·2	310	590·0	351	663·8	1037	1900
229	444·2	270	518·0	311	591·8	352	665·6	1093	2000
230	446·0	271	519·8	312	593·6	353	667·4	1100	2012
231	447·8	272	521·6	313	595·4	354	669·2	1148	2100
232	449·6	273	523·4	314	597·2	355	671·0	1200	2192
233	451·4	274	525·2	315	599·0	356	672·8	1300	2372
234	453·2	275	527·0	316	600·8	357	674·6	1400	2552
235	455·0	276	528·8	317	602·6	358	676·4	1500	2732
236	456·8	277	530·6	318	604·4	359	678·2	1600	2912
237	458·6	278	532·4	319	606·2	360	680·0	1700	3092
238	460·4	279	534·2	320	608·0	370	698	1800	3272
239	462·2	280	536·0	321	609·8	371	700	1900	3452
240	464·0	281	537·8	322	611·6	380	716	2000	3632
241	465·8	282	539·6	323	613·4	390	734	2100	3812
242	467·6	283	541·4	324	615·2	400	752	2200	3992
243	469·4	284	543·2	325	617·0	410	770	2300	4172
244	471·2	285	545·0	326	618·8	420	788	2400	4352
245	473·0	286	546·8	327	620·6	426	800	2500	4532

The methods used for the measurement of temperature may conveniently be divided into two groups, termed respectively (*a*) *thermometry* and (*b*) *pyrometry*. There are no definite limits to these two groups, as the ranges of pyrometers and thermometers overlap to a considerable extent, but, as a rule, the term *thermometry* is applied to the measurement of temperatures up to about 300° C. and *pyrometry* to the measurement of higher temperatures.

The principal means of measuring temperature are as follows :—

1. By measuring the increase in the volume of a solid, liquid, or gas and calculating the temperature from the result. This method is chiefly used in *thermometers*.
2. By comparing the optical characters of the light emitted from several substances at known temperatures and from the results preparing a scale which can be extrapolated for higher temperatures. This method is used in *optical pyrometers*.
3. By measuring the changes in the electrical potential or the resistance of an electric circuit when part of the circuit is maintained successively at various known temperatures, and afterwards extrapolating for other temperatures. This method is used for *thermo-couples* and *electrical resistance pyrometers*.
4. By measuring the radiation from the hot substance by means of a calorimeter, thermometer, or pyrometer. In the ceramic industries, a combination of a mirror and a thermo-couple pyrometer is usually employed and is known as a *radiation pyrometer*.
5. By observing the effect of heat in changing the shape of cones, bars, or other *pyroscopes*, the temperature corresponding to such behaviour having previously been ascertained.
6. By the method of mixtures, a ball of metal or other suitable material being heated to the temperature it is desired to measure and then dropped into a calorimeter containing water. The specific heat and weight of the test-piece and the weight and temperature of the water before and after the test being known, the temperature of the test-piece can easily be calculated from the formula on p. 512.

The **thermometers** used in determining the temperature of ceramic materials usually consist of a sealed glass tube containing mercury. If sufficiently long, they may be used to measure temperatures up to about 350° C., or up to 450° C. if the tube is filled with nitrogen, or to 600° C. if an alloy of sodium and potassium is substituted for the mercury.

For some purposes, a thermometer may be used more conveniently if it is provided with a maximum temperature indicator.

Gas thermometers are now seldom used, as they have been replaced by pyrometers which are more convenient. A gas thermometer consists of a bulb of metal, porcelain, or other impervious material, provided with an outlet pipe connected to a sensitive pressure-gauge. The bulb is filled with air or gas and the reading of the pressure-gauge is noted. The bulb is then placed in the furnace, the temperature of which

is to be determined and the pressure-gauge read at intervals until a maximum reading is obtained. The expansion of the gas in the bulb can then be used to calculate the temperature of the bulb.

The **pyrometers** most suitable for high temperatures are of three chief types, namely, electrical, optical, and radiation pyrometers.

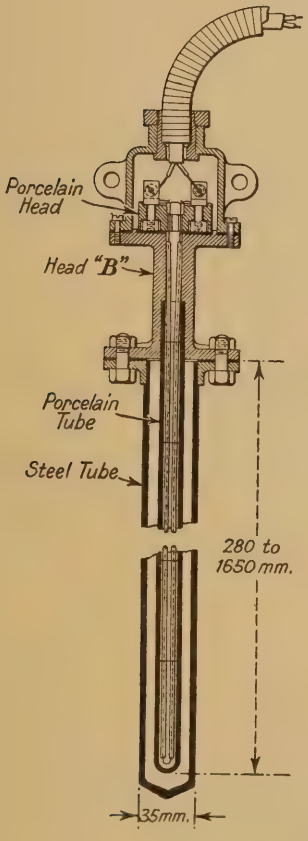


FIG. 47.—THERMO-COUPLE PYROMETER.[1]

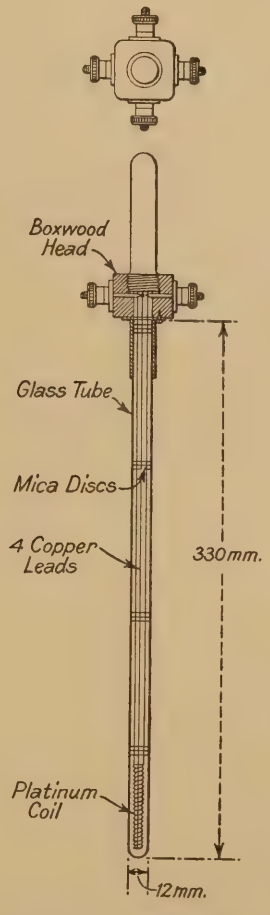


FIG. 48.—RESISTANCE PYROMETER.[1]

Electrical pyrometers are of two distinct kinds :—

(*a*) Those in which the electricity generated in a thermo-couple is measured at different temperatures (fig. 47).

(*b*) Those in which the variations in the electrical resistance of a wire is measured at different temperatures (fig. 48).

Thermocouple pyrometers are based on the fact that when the junction of two

[1] Type of pyrometer supplied by the Cambridge & Paul Instrument Co. Ltd.

dissimilar metals is heated a current of electricity is generated, the voltage depending on the temperature of the junction.

Resistance pyrometers are based on the fact that the electrical resistance of a wire varies with its temperature. Thus, if a coil of wire, which forms part of an electric circuit, is placed in a hot furnace, the difference in resistance is proportional to the temperature of the coil. The wire resistance coil is usually protected by a refractory sheath, and a counterbalancing wire of the same length as the leads is placed in the tube to neutralise their resistance. The resistance of the coil is measured by means of a wheatstone bridge and a galvanometer, the resistance in two arms of the bridge being adjusted until the galvanometer shows no deflection.

Pyrometers of both the thermo-couple and resistance types, in which the scales are graduated so as to read directly in Centigrade degrees, can be obtained from scientific-instrument makers, who should be informed of the purpose for which the instrument is to be used, so that the couple may be made of suitable metals. Such pyrometers can be used to measure all temperatures up to about 1400° C., but above the latter temperature their readings, after prolonged use of the instrument, are uncertain, so that frequent standardisation is necessary.

It is often convenient to attach a continuous recorder to the pyrometer so that a continuous record of the temperature may be obtained.

Optical pyrometers have become very popular during recent years. They are based on the principle that the light emitted by a heated body is proportional to its temperature. The chief types of optical pyrometer are :—

1. Those in which the light from the hot body is varied until it matches a fixed standard. Thus, in a pyrometer devised by Féry, the light is reduced by inserting a standard wedge of dark glass, the position of the wedge being read on an arbitrary scale. In the Le Chatelier optical pyrometer, the intensity of the source of light is reduced by means of an iris diaphragm. In the Wanner pyrometer, the standard light and that from the hot body are viewed through a polariser, a ray from each source being compared and the temperature calculated from the angle through which the analyser must be rotated in order to make both rays match.

2. Those in which the standard light is varied to match the light from the hot body. Thus, if an electric light is used as the standard, its intensity can be varied until it coincides with that of the hot body ; the temperature of the latter is assumed to be proportional to the current flowing in the standard lamp circuit as indicated by a milliammeter. Thus, in the Holborn-Kurlbaum pyrometer, the current supplied to the lamp is varied until the filament is just invisible when viewed against the hot body as a background.

3. Those in which the light from the hot body is just extinguished by interposing a series of standard coloured glasses of different thicknesses as in Lovibond's tintometer or the Wedge pyrometer, in which the hot object is viewed through a wedge of dark-red glass which is slid through a tubular eyepiece so as to insert different thicknesses of glass between the object and the eye until the object is just invisible. The temperature is read off on the scale attached to the instrument. Optical pyrometers are often useful, though not very accurate, except

for strictly comparable conditions and frequent standardisation is necessary. They cannot be used to give a permanent record, and require skilled attention and very careful usage.

Radiation pyrometers may include the optical pyrometers just described, as the latter are based on the light radiated by the hot body. The term radiation pyrometer is, however, chiefly confined to those in which the radiated heat is measured by its effect on the junction of a thermo-electric pyrometer, the radiated heat being focussed either by means of a lens or a concave mirror, and the voltage of the current generated measured by means of a galvanometer the scale of which reads directly in Centigrade degrees as in other pyrometers.

In Féry's radiation pyrometer (fig. 49), a gilt-surfaced concave mirror is mounted on a rackwork focussing arrangement so as to focus accurately the heat rays on to the junction. The Forster radiation pyrometer is so constructed that the focus is "fixed" as in some hand cameras, no adjustment being required if the pyrometer is placed at a sufficient distance from the hot object.

In Féry's spiral pyrometer, the heat is focussed on to a coil of flat metal ribbon to which a pointer is attached. When heated by the rays falling upon it, the coil unrolls and causes the pointer to move over a scale which indicates the temperature of the source of heat. Whilst very convenient it is not so accurate as the type with a thermo-electric junction.

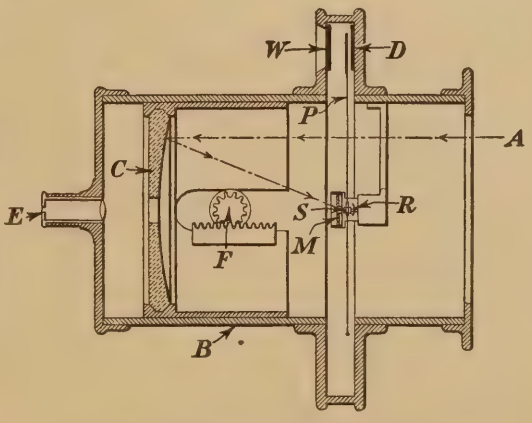


Fig. 49.—Féry Radiation Pyrometer.[1]

Radiation pyrometers are accurate for temperatures over 700° C., but require to be skilfully used, and if roughly handled give erroneous results. The mirrors must be specially cared for, as they will not reflect properly if they become damaged or dirty. They do not deteriorate on prolonged heating in use in the same thermo-electric and resistance pyrometers, and for this reason are very convenient.

Pyroscopes are devices for indicating the temperature of a furnace by the change of shape which they undergo when heated. Strictly, they do not measure the temperature, but the amount of heat which they have absorbed; but whilst this may appear to be objectionable it has certain advantages. In heating ceramic materials, the precise temperature attained by the gases in the furnace is of minor importance; what really matters is the effect of heat on the contents. As most pyroscopes are themselves ceramic materials, their behaviour indicates the effect of the heating and is, therefore, in some respects more satisfactory than that of a pyrometer. (In many cases, both a pyrometer and a pyroscope should be used as the latter will not show a decrease in temperature.)

[1] Type of pyrometer supplied by the Cambridge & Paul Instrument Co., Ltd.

One of the best forms of pyroscopes is the Seger cone, invented by H. Seger, of Berlin, who made various mixtures of finely powdered (100-mesh) silicates in such proportions that they would fuse at different temperatures. The materials were shaped into three-sided pyramids, 5 cm. high and 1·5 cm. on each side at the base,[1] as shown in fig. 50, and the fusion-point (or more correctly the softening-point) was taken to be that at which the apex of the cone bends over and just touches the base.

Table CXV shows the series of Seger cones and the temperatures at which they fuse.[2] It will be seen that the difference between the cones is generally 20°–30° C. It is important that the temperature of the cones should rise at a suitable rate, as if heated too rapidly they will reach a higher temperature than that indicated in the table before bending on account of their being poor conductors of heat. This is no objection in practice, because the ceramic materials with which they are employed have the same low thermal conductivity. The maximum rate of heating is usually taken as 2° C. per minute.

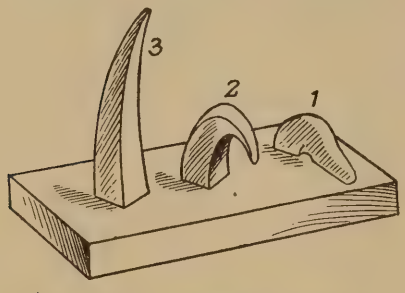


Fig. 50.—Seger Cones.

This type of heat recorder is very largely used in the ceramic industries on account of its cheapness, simplicity, and reliability.

In use, three or more cones of different values are placed near to the object whose temperature is to be estimated and heated up with it. The temperature of the object at different times is then indicated by the bending of cones of different fusing-points. Thus, if it is desired to heat a material to a certain temperature three different Seger cones are used—one to indicate a temperature about 20° C. below what is required and to act as a "warner," the second cone shows when the desired temperature has been reached, and the third cone shows whether it has been exceeded.

Cones are sometimes adversely affected by the gases in a furnace, and especially by carbon monoxide. They should, therefore, only be used under oxidising conditions.

Other pyroscopes of a similar nature are also made. Thus, *calorites* consist of long square bars, one end of which is painted to show the temperature at which it fuses. Holdcroft's *thermoscopes* are similar bars which are placed in a horizontal position in the furnace, their critical point being indicated by their sagging in the middle. A number of suitable thermoscopes may be placed on a fireclay holder in a kiln, and the temperature will be indicated at intervals by the sagging of the bars. Opinions differ considerably as to whether the cones or thermoscopes are the more convenient. *Watkin's pyroscopes* are small tablets which melt at specified temperatures. They are very small and often difficult to see when in use. *Brearley's Sentinel pyrometers* are similar but rather larger. Their critical point is reached when they are completely fused.

[1] For the highest temperatures, a smaller series of cones 1 in. high is used.

[2] The composition of the various cones is given in the same Table.

Fusible metals and salts are also of some value for lower temperatures, but they are not much used in the ceramic industries. They are convenient, however, for standardising pyrometers, etc. The chief salts used and their melting-points are: (i) a mixture of equi-molecular parts of sodium and potassium chlorides (650° C.), (ii) sodium chloride (800° C.), (iii) anhydrous sodium carbonate (850° C.), (iv) anhydrous sodium sulphate (900° C.), (v) sodium plumbate (1000° C.); (vi) anhydrous potassium sulphate (1070° C.), and (vii) anhydrous magnesium sulphate (1150° C.).

The fusion-points of sheets or strips of various metals is shown in Table CXXXIX, due to Seger.

TABLE CXXXIX.—*Melting-Points of Metals and Alloys*

Metal or Alloy.	Melting-Point, ° C.
800 parts of silver, 200 parts of copper	850
950 ,, ,, 50 ,, ,,	900
Pure silver	954
400 parts of silver, 600 parts of gold	1020
Pure gold	1074
950 parts of gold, 50 parts of platinum	1100
900 ,, ,, 100 ,, ,,	1130
850 ,, ,, 150 ,, ,,	1160
800 ,, ,, 200 ,, ,,	1190
750 ,, ,, 250 ,, ,,	1220
700 ,, ,, 300 ,, ,,	1225
600 ,, ,, 400 ,, ,,	1320
500 ,, ,, 500 ,, ,,	1385
Platinum	1775

Trials made of **clay** and dipped in a glaze-mixture are often used to ascertain the progress of the heating of pottery ovens. The glossiness and colour of the glazed pieces are a sufficient indication to a skilled burner of the progress of the firing. This apparently crude and uncertain method has enabled potters' firemen for many years to control the firing of kilns with remarkable success.

A simple means of ascertaining whether the heating of a kiln filled with bricks, tiles, or some other ceramic ware has been effective, is to measure the distance between the top of the contents of the kiln and the top of the kiln itself. As most bricks will shrink $\frac{1}{2}$ inch per linear foot in burning, it is clear that in a kiln filled with bricks to a height of 8 feet, the loss in height after the firing is completed will be $\frac{1}{2} \times 8 = 4$ inches, and that by measuring the shrinkage at intervals the progress of the heating

may be ascertained. Though crude, this method is in regular use and proves to be satisfactory.

Wedgwood—the great potter—used to measure the contraction of small test-pieces which were drawn from the kiln at intervals and their diameter measured in a V-shaped gauge. By substituting calipers for the gauge used by Wedgwood the contraction of larger and more conveniently shaped pieces can be accurately measured. Strict accuracy of size is very important where the articles are to be used in conjunction with others, as in the ceramic portions of switches and other electrical fittings, though it is seldom practicable to measure the contraction of individual pieces whilst they are in the oven or kiln; when the heating is finished, it is obviously too late for such measurements to be used in controlling the firing.

There is great need for a means of determining the changes in volume which take place in ceramic articles whilst they are in the kiln, so that the heating may be regulated accordingly. Unfortunately, there seems to be no suitable means of obtaining this information at the time when it is most needed. Pyrometers and other instruments for ascertaining the temperature of the kiln are exceedingly useful, but they give only indirect information and are, therefore, of less value than is desirable. The difficulty is greatly increased when articles are burned in saggers, as it is then almost impossible to gain access to them, or to know precisely what is occurring to them at any given moment. In this respect, so much has to be left to chance, and to the subconscious judgment of the firemen, that the art of kiln-control is far ahead of the science.

CHAPTER XIII

THE EFFECT OF HEAT ON CERAMIC MATERIALS

In the previous chapter, the general effect of heat upon various substances has been considered; this chapter is devoted to the effect of heat upon ceramic materials—a matter of special importance as they are all subjected to heat at some stage in their manufacture, and some ceramic materials owe their value to their resistance to heat when in use.

The effects of heat upon ceramic materials may be conveniently considered in relation to—

1. *Drying* clays and other ceramic materials, both in the natural state and after they have been made into articles.

2. *Burning* or *firing* ceramic materials and articles made from them, this subject being sub-divided into (*a*) smoking, (*b*) decomposition, (*c*) the "full fire" stage of heating, and (*d*) the finishing stage, including "soaking" and "vitrification."

3. The *effect of withdrawing heat, i.e.* cooling the fired products in such a manner as not to damage them.

4. The effects of *excessive heating*, as shown by "squatting," fusion, boiling, volatilisation, etc.

In addition, the effects of heat on ceramic materials may also be considered in respect of the resulting changes in the volume of the material as a whole or of its component grains, in the thermal conductivity, specific heat, refractoriness, and resistance to sudden changes in temperature.

Effects of Heat in Drying

The effects of heat during drying are partly physical and partly chemical in character. The resulting changes are practically the same as occur when the drying is effected at atmospheric temperature, the water being removed by a current of dry air. The drying is, however, greatly facilitated and accelerated by the application of a gentle heat. The changes which occur in drying have been fully described in Chapter VII.

In actual practice, the drying of ceramic articles is not usually completed in the drying appliances, even when the articles appear to be quite dry; the remaining water is removed when they are in the kiln or oven.

Effects of Heat in Firing

The effects of heat in burning or firing ceramic articles are most conveniently studied by considering separately each stage in the process, commencing with the effect of a very gentle heat—technically termed " smoking "—and proceeding until the final or " finishing stage " of the firing is reached. It must, of course, be understood that there is no sharp line of demarcation between these various stages, the effects of heat being continuous, so that the division of the firing into several " stages " is wholly empirical.

Smoking.—When a piece of clay or an article made of clay and allied materials which has been dried to the extent customary in manufacture is placed in a kiln or oven, the first effect of the heat is to remove any moisture still remaining in the material. It is by no means unusual for 5 per cent. of water, equivalent to 1 cwt. or 3000 cubic feet of steam per ton of goods, to be present in the " dried " articles taken to the kiln and to be evolved as steam during the first stage of heating. For the steady evolution of this enormous volume of vapour without any damage to the contents of the kiln, it is very important to provide ample ventilation and to take precautions that the temperature shall not rise too rapidly, as, otherwise, the goods may be cracked by being unable to withstand the pressure of the steam produced in their interior and unable to escape with sufficient rapidity through the small pores in the articles.

The first or " smoking " stage of the burning of ceramic materials is finished at a temperature of about 120° C. When this temperature is attained throughout the kiln and its contents, the whole of the water will have been vaporised and the second stage of heating may then be commenced.

At so low a temperature as 120° C. very few chemical changes occur, other than those produced when the heating is effected by waste gases bearing products of combustion from another part of the kiln. Such gases often contain sulphuric trioxide which can combine with any lime present in the clay and, in the presence of moisture, may form calcium sulphate in the form of a white deposit or " scum " on the surface of the goods.

The removal of the water is the chief change which occurs during the " smoking " ; other changes which may be produced simultaneously include the following :—

(i) *Shrinkage* occurs as a result of the particles approaching each other on the removal of the water which previously separated them. The extent of this shrinkage on drying is described in Chapter VII.

(ii) The *porosity* is increased, because the pores of the material at the end of the smoking stage are filled with air instead of water, as described on p. 75. The change in porosity also causes a change in the apparent density (p. 205).

(iii) The *permeability* is also increased for the same reason (p. 89). A mass of clay when saturated with water is practically impervious, but, when dry, it may allow gas or water to pass through readily.

(iv) The *colour* may change slightly (p. 107), most clays becoming rather lighter when perfectly dry. Other materials change to a greater or less extent.

(v) The *hardness* of clays is increased (see Chapter III), but non-plastic materials usually become more friable.

(vi) The *compressive strength* of clay wares increases on drying, but the strength of non-plastic materials usually decreases. Hence, non-plastic materials must be very carefully handled in the dry state as they are liable to be very friable (see Chapter IV).

Other minor changes in thermal and electrical conductivity, etc., may also occur.

At the end of the " smoking " stage, ceramic materials are either (*a*) harder than before, if made largely of clay or containing some other colloidal gel, or (*b*) more friable, if made of non-plastic materials. The latter may, however, be hard if water-glass has been used as a bond. In either case, they have the same properties as the thoroughly dried material, the other effects of heat at this stage being usually negligible.

The **decomposition stage** is the second stage in the burning or firing of ceramic materials ; its range of temperature extends from about 120° C. to about 900° C., and in this interval many important chemical and physical actions occur. It is usually essential at this stage that the temperature shall rise very steadily, though the rate of heating may vary within wide limits with different materials. Slowly at 120° C. and much more rapidly at 400°–600° C., minerals containing chemically combined water are dissociated, the water being evolved as steam. The most important of these ceramic materials is *clay*, which is completely decomposed between 500° and 700° C., and usually below 600° C. as described on p. 350. Various other hydrous silicates and alumino-silicates which may be present are also decomposed. *Limonite* (p. 418) loses its combined water at about 500° C., *haematite* (p. 418) being formed. Some forms of hydrous alumina lose their combined water at one temperature ; others, including *bauxite*, retain a portion of it at a much higher temperature (p. 340). The numerous hydrous minerals which occur in very small quantities also lose their combined water during this stage of burning.

Allotropic changes also occur in some of the minerals present. Thus, at about 575° C. α-quartz is converted into the β-variety, and at a higher temperature quartz is converted into other forms having a lower specific gravity (p. 216).

As the temperature continues to rise to above 700° C., other minerals are dissociated ; some of the carbonates (such as limestone, chalk, magnesite, and dolomite) evolve carbon dioxide and so are converted into oxides (p. 490).

Any sulphides present, such as pyrites, muscovite, etc., are partially decomposed, a portion of the sulphur being oxidised and evolved as a gas, whilst the remainder is only evolved at a higher temperature.

At about 900° C., and sometimes at a lower temperature, any carbonaceous matter present will be decomposed, usually producing a black charred mass, which is converted into carbon-dioxide gas if the atmosphere in the kiln or oven is sufficiently oxidising. Any shale oil and volatile hydrocarbons are evolved as hydrocarbon gases which may burn and produce carbon-dioxide gas and steam.

Gypsum and other sulphates are partially decomposed at a temperature of about 800° C., the sulphur being completely expelled at temperatures above 900° C.

Any ferrous iron compounds will, if the atmosphere in the kiln or oven is sufficiently oxidising, and the contents are sufficiently porous for that atmosphere to penetrate properly, be converted into ferric compounds.

Many other minor reactions will also occur in which minerals present in proportions too small for them to be considered separately are decomposed in a manner similar to some of those previously mentioned.

At a temperature between 120° and 900° C., many chemical changes commence which are not completed until a higher temperature is attained, but having once started they proceed gradually and are completed (as far as this is permitted) in the next stage of the burning. Thus, the bases present as impurities in the material or produced by the action of heat on carbonates, etc., begin to attack the silica and alumina also present and, conversely, the acidic materials present in basic ones react with the bases. By this means, fusible silicates and alumino-silicates are produced and if they are sufficiently numerous and have a sufficiently low melting-point, an appreciable amount of glassy or vitreous matter will be formed to surround many of the individual particles and partially to fill the pores or interstices between them. This is more fully considered on p. 551.

Apart from the reactions which result in the production of a fused glassy material, the chief changes which occur at this stage are oxidation processes which depend for their satisfactory completion on the presence of an ample supply of air. As these changes occur in the order of their affinity for oxygen, the heating must be properly controlled or undesirable reactions may occur whilst desirable ones remain incomplete. Thus, carbon has the greatest affinity for oxygen, so that in a highly porous and heat-resistant body the oxidation of compounds of iron, sulphur, etc., will not be completed until all the carbonaceous matter has been fully oxidised, and where the latter is present in large quantities it is important that the temperature should rise sufficiently slowly to remove the carbonaceous matter entirely before too high a temperature is reached. Otherwise, as the heat is nearly always applied externally to the materials,[1] the exterior may be raised to such a temperature that partial fusion occurs and the exterior pores are thereby sealed before all the carbonaceous gases can escape. The result of such sealing will be shown at a later stage by the articles being swollen or bloated by the pressure of gases in their interior. The appearance of the articles may also be spoiled by the charred material remaining behind and being incapable of oxidation because the air in the kiln cannot gain access to it on account of the sealed pores.

It is out of place in this volume to discuss the various methods employed to burn different goods properly at this stage; further information will be found in the author's works, *The Clayworkers' Handbook*; *British Clays, Shales, and Sands*; *Refractory Materials: Their Manufacture and Uses*; *Modern Brickmaking*, etc.

The nature of these oxidation processes need not be described in detail as they have been discussed on pp. 491–492.

Various physical changes also occur during the decomposition stage of firing, these

[1] The only exceptions being clamp bricks and some articles in which sawdust or other combustible matter forms an essential part of the material of which they are made.

being partly as a result of the chemical changes mentioned. The chief of the physical changes are as follows :—

Changes in volume occur as a result of the following causes : (*a*) the water which previously separated the particles having been removed, the remaining particles draw closer together. The expulsion of " combined water," carbon dioxide, sulphur oxides, etc., has a similar effect and produces a further shrinkage which will be more or less pronounced according to the extent to which they occur ; (*b*) a reduction in volume, or shrinkage, also occurs in some materials as a result of allotropic changes brought about by the heat, as when magnesia is slowly converted into periclase, though this change is usually much more pronounced at higher temperatures (p. 551) ; (*c*) an expansion or increase in volume occurs in some materials containing, or largely composed of silica, due to allotropic changes caused by heat (p. 568).

Changes in porosity occur to a varying extent during this stage. The porosity usually increases until near the end of this stage of the firing, though when the proportion of readily fusible matter is sufficiently large, the porosity may be reduced at temperatures above 800° C. Further information on changes in porosity of ceramic materials when heated will be found in the section on *Porosity* in Chapter II.

The *permeability* generally increases during this stage (see the section on *Permeability* in Chapter II).

Colour changes frequently occur in this stage of firing as a result of the chemical reactions which occur. Clays generally become lighter in colour unless they contain much iron—in which case the colour is intensified by the oxidation of the iron with the production of a bright red colour. Iron pyrites is so difficult to convert into red ferric oxide in the presence of clay that it usually forms black spots of fused ferrous silicate. The colour changes are described in the section on *Colour* in Chapter III.

In some articles made of ceramic materials the changes in colour produced by heating is not important. In other cases, on the contrary, the value of articles such as red facing bricks, roofing and floor tiles, terra-cotta, etc., is largely determined by their colour and it is, therefore, important that, with them, this stage of heating should be controlled with special care and skill. Such articles are fired almost solely with reference to their colour, the other properties required receiving but little attention and the burning may be completed in this stage when the colour is spoiled by heating the articles to higher temperatures. Hence, red bricks and similar goods are finished at a temperature of 900°–1000° C.

The *hardness* of ceramic materials usually increases at temperatures between 120° and 900° C. Clay is changed from a soft plastic state in which it is used when shaping the articles into a hard stony material which has quite different properties. Colloidal gels and other binding agents are usually hardened and to some extent are fused, thus cementing together the non-plastic particles, though this cementation may not be completed until a later stage of firing. The changes in hardness which occur are discussed at length in the section on *Hardness* in Chapter III.

The *strength* (when cold) of ceramic materials is increased during this stage of the burning because the hardness increases and the bonding material becomes firmer. The chief increase in strength—except when the more readily fusible substances are

present—occurs in the next stage when vitrification proceeds rapidly, but a notable increase often occurs during this stage as a result of the commencement of vitrification. The strength of the materials at the high temperature may be less than that at lower temperatures, V. Bodin having found that many ceramic materials, when tested whilst hot, decrease in strength up to 800° C. and then increase again as the temperature rises to 1000° C. The strength of materials at different temperatures is discussed in detail in Chapter IV.

Changes in the *specific gravity and apparent density* of ceramic materials occur at this stage as a result of various chemical changes and the formation of various allotropic modifications of the original substances. Thus, the specific gravity of silica begins to decrease, whilst that of magnesia rises. Clay which has been heated to expel all the combined water does not change much in specific gravity when heated to 900° C., unless it is very impure and contains a large quantity of free silica, in which case the latter causes a decrease in specific gravity. The changes in specific gravity are discussed in detail in Chapter V.

As the porosity changes, the apparent density is also modified according to the extent of the change (see also Chapter V).

The *thermal conductivity* and *specific heat* of ceramic materials generally rise as the temperature increases (pp. 584 and 594).

The *electrical conductivity* of ceramic materials increases with the temperature (Chapter XIV), whilst their resistivity decreases. Consequently, ceramic materials become weaker insulators when heated than in the cold state.

Summarising, it may be said that the changes which take place in the " decomposition stage " of firing are the results of oxidation and chemical reactions between the various bases and acids, though where the proportion of soda and potash is small the latter reactions do not make much progress. In some of the very impure clays used for brickmaking, etc., sufficient soda, potash, and lime are present to ensure a considerable amount of glassy compounds (due to the combination of these bases with silica) being formed and the resulting products are then hard, dense, and sonorous when struck. When a brilliant red colour is desired, the firing must usually be finished before much vitrifiable material has been formed as it tends to produce an unpleasant brown instead of the brilliant terra-cotta red which is so much desired in some clay products.

In the case of some pottery ware made of natural or artificial mixtures of clay and calcium carbonate, the firing is finished at about 900° C., as a much higher temperature would cause the formation of fused calcium-iron silicates. The firing of ceramic articles made of basic or highly aluminous materials is not completed in this stage, so must be considered later.

Plumbiferous glazes and those rich in borax are completely fused in this stage of burning, but do not call for any special comment except in so far as they give some indication (by analogy) of the general nature of the fusible compounds in other ceramic materials.

The **full-fire stage** in burning ceramic ware commences at that temperature at which the kiln or oven may be heated as rapidly as is possible without serious risk

of damage to its contents. In the case of the most impure clays, it probably commences at about 800° C., but it is usually safer to regard it as commencing at 900° C. with some reservation with respect to the more fusible clays, glazes, etc.

The " full-fire stage " is in every respect an intermediate one and in it the various chemical and physical changes which commenced in the prior, or decomposition stage continue at a more rapid rate, some of them reaching completion. In the " full-fire " stage, the production of fused material increases rapidly and the more mobile and fusible glasses produced readily penetrate the pores in the more refractory material, dissolving the latter and so producing a still further quantity of the fused glass, slag, or " vitrified matter."

The chemical changes which occur in this stage are not essentially different from those in the latter part of the previous stage. They consist chiefly in the combination of the bases or basic silicates with a further amount of silica. The higher the temperature attained in this stage, the more complete will be the chemical reactions between the basic and acid materials present and the greater the amount of silica entering into solution in the fused portion of the material. These reactions are more conveniently considered separately (see *Vitrification*, p. 551).

The *porosity* of the materials continues to increase and reaches a maximum in this stage, but in the following one it begins to decrease as a result of vitrification, so that the end of the full-fire stage is sometimes considered to be that at which the porosity reaches a maximum. It is, however, very difficult to prescribe any definite upper limit to the full-fire stage, because it differs so greatly with different materials and is, in itself, somewhat indefinite in character.

The *permeability* also reaches a maximum in this stage, but is subject to the same limitations.

The *colour* of any ferric oxide or allied compounds assumes a maximum brilliancy in this stage, but as the amount of vitrified matter increases, the colour is considerably modified by other chemical changes which take place.

The *strength* of ceramic materials (after cooling) increases as the temperature of firing rises and continues to do so during this and especially during the next stage, when a considerable increase occurs on account of the vitrification of the bond (see Chapter IV). The strength at high temperatures, which, according to Bodin, decreases with many materials up to 800° C., rises during this stage and attains a maximum about 1000° C. The maximum strength at high temperatures generally corresponds with the point of maximum porosity ; this must not be confused with the maximum strength at ordinary temperatures which is often greatest when the porosity is least (p. 152).

The *specific gravity* of some of the materials changes in the same manner as in the decomposition stage, but usually at a more rapid rate as the temperature is greater. The changes which occur in the *thermal* (p. 584) and *electrical conductivities* (p. 608) also continue in the same general manner, but more rapidly, the latter always and the former generally increasing during this stage of burning.

The **finishing stage** of the firing of ceramic ware is that in which the desired reactions and other changes are completed or have progressed to such an extent as

to produce articles or materials having the requisite properties. In this stage the temperature of the kiln or oven does not rise appreciably above that of the full-fire stage. On the contrary, it should usually be maintained as constant as possible. For this reason, this period is often known as the *soaking stage*, the materials or articles being regarded as " being soaked in the heat " until it has penetrated completely through them in much the same manner as water will penetrate a porous material immersed in it for some time.

The purpose of this prolonged heating or soaking at an almost constant temperature is to enable the various changes which have commenced in previous stages to be completed or at any rate to progress to an extent which will produce the desired properties in the product. If the temperature is allowed to rise rapidly until the firing is finished there is always a danger—except with the most refractory materials —that the articles will be distorted or their colour or other desirable properties will be spoiled by overheating. This serious defect is largely avoided by maintaining the temperature at an almost constant level during the last stage of firing, as this procedure enables the process to be more satisfactorily and readily controlled.

This prolonged heating or " soaking " at a suitable high temperature may have the following effects :—

(*a*) It may increase the amount of fused matter and, consequently, the amount of chemical action between the fluxes and the more refractory constituents, thus producing a larger amount of vitrified or glassy material which will gradually fill the interstices between the other particles, rendering the whole impermeable, as in the case of stoneware, or even translucent, as in porcelain.

By allowing ample time for the various chemical reactions to occur, prolonged heating of a ceramic material at the close of the firing imparts great stability to the material as a whole and enables a state of stable equilibrium to be attained. This is very important, when the product is to be reheated in use, as an unstable product —due to insufficient " soaking "—will continue to undergo various physical and chemical changes which may have very serious consequences. The heating must not, of course, be prolonged to such an extent that undue distortion or loss of shape (see *Squatting*, p. 560) occurs. It is in the avoidance of this defect that the skill of the fireman is revealed, for the chemical reactions which are facilitated by the burning process must be stopped before they have proceeded too far. In other words, in the production of ceramic ware, most of the chemical reactions possible between the various constituents can never be completed, as that would render the material quite useless for the purpose for which it is intended. In this sense, as J. W. Mellor has pointed out, the chemistry of the firing of ceramic substances is a chemistry of arrested reactions. Unless the arrest takes place within a very narrow range of time or temperature, the product will be spoiled, hence, the enormous importance of as complete a control as possible over the kilns or ovens in which the burning is effected.

In most of the chemical processes employed in other industries the principal object is to complete the reaction as rapidly as possible consistent with obtaining the maximum yield of the desired product, but this is not the case in firing ceramic wares, as the possible reactions cannot be allowed to proceed to completion, but must

be stopped at a point which enables the product to possess the complex series of properties which are essential to its use to the best advantage. Anyone with even a small knowledge of chemical reactions knows how difficult many of them are to arrest when they take place at the temperature of boiling water, and can realise how much more difficult it is to arrest such reactions when occurring at 1000° C. or above without damage to the product. Yet such a stoppage must be effected promptly and at precisely the right time, especially in the manufacture of some of the most delicate wares.

(*b*) It may permit the crystallisation of some of the constituents. Thus, sillimanite (p. 413) may be formed in clay goods, cristobalite or tridymite (p. 426) in siliceous materials, periclase (p. 428) in magnesia bricks, etc. In some cases, the production of a mass of felted crystals gives the mass an added strength and a greater resistance to sudden changes in temperature. In others, the crystals are important because they are the most stable form of material under the conditions which it will be used. In glazes and sometimes in binding materials, the production of crystals is undesirable and is regarded as a defect.

(*c*) It may cause the volatilisation of alkalies (p. 561) and thus increase the refractoriness of the residual material, though this can only occur to a very small extent in the soaking stage of burning ; it is more important when ceramic products are subjected to prolonged heating at a high temperature during use.

Other effects of prolonged heating are described on p. 562.

The length of the soaking period will, of course, depend on the desired qualities in the finished product, and owing to the complexity of most ceramic materials it must usually be found by trial based on experience.

Vitrification.—One of the chief purposes of a prolonged finishing stage in the burning of ceramic materials and articles is the production of a suitable amount of vitrified or glassy material which will surround the remaining particles and fill the interstices between them to a suitable extent, dependent on the properties desired in the finished product. In the case of building bricks and earthenware, it is sufficient if the more refractory particles are united sufficiently firmly to produce a mass of ample strength. In stoneware, engineering bricks, and acid-resisting materials, a larger proportion of vitrified material is required so as to fill the pores and prevent the permeation of liquid into the article, and in porcelain and china-ware a still larger proportion of vitrified material is needed so as to produce a translucent material without loss of shape. The temperature at which a sufficient amount of vitrification is reached will depend on the nature and proportion of the fluxes and of the most fusible materials present. It will obviously be reached earlier with a fusible clay or with one rich in fluxes than with a highly refractory material such as kaolin, magnesite, or bauxite.

Vitrification commences when the fusion-point of the least refractory constituents (or of the most fusible product of any reactions which may have occurred) is reached, but owing to the complex nature of ceramic materials no single temperature can be stated as that of the commencement of vitrification. With some very fusible clays and glazes it is as low as 450° C., whilst some highly refractory materials, such as

magnesia and alumina, show no signs of fusion below 2000° C. With most of the crude clays used in the ceramic industries the commencement of vitrification appears to occur at about 750°–800° C.

A readily fusible substance present in the material may be the first to fuse and so start the vitrification, but it is more usual for a sodium or potassium salt to decompose and combine with the silica, forming a fusible silicate. This fused basic silicate will, as the temperature rises, act as a solvent for some of the other silicates and bases present, and the molten material thus forms a liquid in which the various substances can react far more rapidly than when all are in the solid state. By this means, fused complex compounds, eutectics, and solid solutions are formed. These changes, which have been described in Chapter XI, increase in extent and velocity as the amount of vitrified material increases and the temperature rises, until—unless its progress is previously arrested—a point is reached when there is so much fused material present that the mass is unable to retain its shape and loss of shape occurs (see *Squatting*, p. 560), and if the heating is still further continued at a suitable temperature, the whole of the material is reduced to a molten or liquid state and forms, when cooled, a glass or slag.

The rate of vitrification is very slow at low temperatures, but increases rapidly at temperatures above 1200° C. (sometimes at a much lower temperature), except with the most refractory materials, some of which can only be melted in the intense heat of the electric arc.

The chemical changes which occur during the production of vitrified material cause various physical changes to take place simultaneously. Thus, the volume of the material changes as the interstices are filled and the solid material is dissolved, and also as products of different specific gravity are formed. The porosity and permeability decrease as the pores are filled with the molten material. The strength of the hot material decreases as the amount of fused material increases, the mass becoming more mobile, but when cold the strength is increased as a result of the larger amount of fused glassy matter produced acting as a bond uniting the other particles firmly together.

The multitudinous changes which occur simultaneously with the vitrification are too numerous to be described in detail; much information relating to them will be found in the earlier chapters in this volume.

The term *vitrification range* is applied to the range of temperature between the commencement of fusion and the loss of shape due to the production of vitrified material. It varies according to the nature of the substances present. Some clays, such as those containing a large quantity of lime or soda compounds, have a very short vitrification range on account of the fluidity of calcium and sodium silicates and alumino-silicates; in some such clays the range may be as low as 30° C., whilst in some refractory clays the range may be 300° C. or more. Table CXL, due to Wheeler, shows the vitrification range of different clays.

In clays and in other materials, the vitrification range depends chiefly on the nature of the fluxes present. In siliceous materials bonded by lime or in calcareous or magnesic materials bonded with clay the range will obviously be short, whilst if a

moderately refractory clay is used as a bond for a siliceous material, a longer vitrification range will be obtained. Magnesia is usually regarded as producing the longest range of vitrification obtainable with siliceous materials, especially if clay is present, as the product is more viscous than that of the corresponding lime- or alkali-compounds, and as it does not penetrate the pores so readily its rate of attack is much slower. The property does not appear to be present in magnesia-soda glasses which are not more viscous than those in which the magnesia is replaced by lime.

TABLE CXL.—*Vitrification Range of Clays*

Nature of Clay.	Vitrification Range.	
	° F.	° C.
Very calcareous clay	75	24
Very impure clays and shales . . .	300	149
Less impure clays and shales	350	176
Fireclays, potter clays, kaolins . . .	400	204
Some china clays and pure fireclays . .	500	260

Finishing Temperature.—The temperature at which the firing of ceramic materials or articles are finished depends on the nature of the contents, but in any case it will be below that at which the vitrification of the product is so far advanced that serious loss of shape occurs.

Different materials and articles require different finishing temperatures for reasons already stated, and even articles of one class, such as building- and fire-bricks, cannot all be finished at the same temperature on account of variations in the composition of the materials of which they are composed. The following notes are intended to give some idea of the temperatures used for different articles :—

Building bricks, *roofing tiles*, and *terra-cotta* are burned at various temperatures according to their composition and the type of the product required. Bath-bricks, "rubbers," and similar soft articles are merely baked at a moderate red heat (about 800° C.). Most building bricks, roofing tiles, and terra-cotta are fired at about 900°–1000° C., at which temperature only just sufficient vitrified matter is present to surround the particles and unite them strongly together. Engineering and vitrified bricks, which contain a much larger proportion of vitrified matter, are fired at 1000°–1300° C. (see Table CXLI).

Salt-glazed articles must be fired at a higher temperature than building bricks, because the salt and clay will not combine satisfactorily at temperatures below 1180° C. (Cone 5*a*).

Earthenware is a term applied to articles made of so many kinds of clay and mixtures of clay with other materials that no satisfactory figures can be given for its finishing temperature. Some of the most crude earthenwares and some majolica wares are finished at 790° C. (Cone 015*a*), whilst white ware is finished at 1140°–1300° C. when in the biscuit state and at 1080°–1300° C. when glazed. Between these wide limits it is impracticable to give closer figures unless all the required

properties are known with great exactitude, and as much of this information is rightly regarded as private property, it cannot be published at present.

Earthenware is required to have a porous body to which the glaze will adhere readily. The ware should also be strong enough to withstand ordinary usage, but it need not be vitrified. It is, therefore, burned at a lower temperature than porcelain ware, though the temperature reached in some kilns in which the best qualities of earthenware are burned approaches very closely to the finishing temperature of porcelain.

In the manufacture of earthenware and porcelain, the ware is first fired in the unglazed state, producing *biscuit*, which is then glazed and refired.

Stoneware is required to contain more vitreous material than earthenware and must, therefore, be fired under conditions which ensure the requisite amount of vitrification. The best qualities of stoneware are quite devoid of porosity even apart from the glaze. The nature of the glaze sometimes affects the temperature at which stoneware is finished as it is customary to apply the glaze to the dried ware, whilst earthenware is made into biscuit and then glazed. The term " stoneware " includes many varieties of ware ; that to which it is chiefly applied in this country is usually finished at a temperature of about 1200°–1250° C. (Cones 6*a*–8).

China and other kinds of *porcelain* are heated so as to secure the maximum amount of vitrification without loss of shape. The finishing temperature is naturally largely influenced by the nature of the materials used and this accounts for the great variations shown in Table CXLII. Some " soft " porcelains formerly made were fired at still other temperatures. Like the better qualities of earthenware, it is usually necessary to fire porcelain articles twice—once in the unglazed state and afterwards when glazed. The latter temperature may be lower than the former if the purposes for which the ware is to be used permit this.

Glazed ware may be fired in either one or two periods ; in the so-called " single-firing " process, the glaze is applied to the unfired ware and the burning must then be controlled in a manner similar to that described for earthenware, but continued to such a higher temperature as may be necessary to fuse the glaze completely and cause it to spread uniformly over the glazed surface. In the so-called " glost-firing," the glaze is applied to the fired or biscuit ware and the glost-firing can, therefore, be effected much more rapidly as the only changes of importance which are required to take place are those which occur in the glaze.

Glazes are required to be completely fused and to become sufficiently mobile that they distribute themselves uniformly except in those cases where an irregular distribution is required as a means of decoration. As the various chemical reactions should proceed to completion in the fused glaze, the temperature may usually be raised fairly rapidly, but care must be taken not to spoil the glaze by overheating it, especially if it has been applied to unfired ware.

The retention of a suitable oxidising or reducing atmosphere during the firing is very important in glazed ware and especially in the case of coloured glazes, for many substances used as glaze-stains are profoundly modified in colour by the nature of the atmosphere in which they are heated. Thus, chromium compounds are green in a

reducing atmosphere, but red or buff in an oxidising one ; lead glazes may be blackened in a reducing atmosphere, and manganese and cobalt compounds form bubbles of oxygen if the glaze is heated too long in an oxidising one. Hence, it is impossible to fire all kinds of colours at one time in a kiln. Steady firing is essential for glazes, or the ware may be blistered or " feathered." Very slow firing is detrimental to glaze, so that the firing should be as rapid as possible without damaging the ware.

Tables CXLI and CXLII show the finishing temperatures for various classes of goods :—

TABLE CXLI.—*Finishing Temperature for Building Bricks, Tiles, etc.*

Type of Ware.	Finishing Temperature.	
	Seger Cone.	° C.
Red bricks, and tiles rich in iron and lime	015*a*–01*a*	790–1080
Red bricks, and tiles free from iron and lime	1*a*–10	1100–1300
Glazed bricks	6*a*–9	1200–1280
Staffordshire blue bricks	10–14	1300–1410
Clinkers and paviours	1*a*–10	1100–1300
Vitreous tiles	5*a*–6*a*	1180–1200
Salt-glazed bricks, drain pipes, etc.	5*a*–10	1180–1300

TABLE CXLII.—*Finishing Temperatures of Earthenware, etc.*

Type of Ware.	Finishing Temperature.	
	Seger Cone.	° C.
Whiteware, biscuit	3*a*–10	1140–1300
Whiteware, glost	01*a*–10	1080–1300
Easy earthenware, biscuit	4*a*–5*a*	1160–1180
Hard earthenware, biscuit	5*a*–6*a*	1180–1200
Easy earthenware, glost	03*a*–1*a*	1040–1100
Hard earthenware, glost	2*a*–3*a*	1120–1140
White stoneware (soft glaze)	09*a*–03*a*	920–1040
White stoneware (hard glaze)	1*a*–10	1100–1300
Stoneware with salt glaze	5*a*–10	1180–1300
Majolica ware	015*a*–05*a*	790–1000
China biscuit ware	9–10	1280–1300
Hard porcelain ware	7–20	1230–1530
Hard porcelain glaze	13–16	1380–1460
Glass colours	022–021	600– 650
Easy enamel kiln	020–018	670– 710
Medium enamel kiln	017–016	730– 750
Hard enamel kiln	016–015*a*	750– 790
Porcelain colours and lustres	022–010*a*	600– 900

Refractory articles such as firebricks, crucibles, retorts, etc., should usually be fired at a temperature higher than that at which they are to be used. If this is done, any further heating to a lower temperature cannot have very much adverse effect. In practice, however, it is customary to burn the goods till they are sufficiently hard and have a good " ring," and it is only within the last few years that the necessity for finishing these articles at a sufficiently high temperature has been properly appreciated.

It is not always necessary to burn firebricks at the maximum temperature reached by the materials in connection with which they are to be used and in some cases it is impossible to do so, as the bricks, if heated to that temperature, would soften and lose their shape, whereas they are quite satisfactory when only one face or side is raised to that temperature as in actual use. Nevertheless, it is always desirable to burn firebricks at the highest practicable temperature, and it is also important to maintain that temperature for a sufficiently long period (p. 550) in order that the various desirable changes may take place. A mistake which is commonly made is to reach a high temperature, but not to maintain it for a sufficiently long time, the firing being stopped before the heat has had time to penetrate the articles sufficiently.

Fireclay bricks are frequently finished at about Cone 5*a* (1180° C.), but this is too low. The better qualities should be fired to Cones 7–12 (1230°–1350° C.), whilst still better ones would be obtained if fired to Cone 14 (1410° C.) or still higher temperatures, though these are seldom reached. In each case, the kiln or oven in which the bricks are burned should be maintained at a temperature within about 50 degrees of the maximum for at least 24 hours so as to ensure a sufficient " soaking."

Silica bricks of the best qualities ought to be fired at Cones 14–18 (1410°–1500° C.), including a soaking at or near the maximum temperature for at least 8 to 10 hours. A still higher temperature (up to Cone 26 or 1580° C.) is desirable with a soaking period of 24 hours, but this is seldom done on account of the great cost of reaching and maintaining so high a temperature, and many commercial silica bricks are only fired to Cones 9–12 (1280°–1350° C.).

Bauxite bricks should also be fired at a very high temperature, preferably between Cones 14–18 (1410°–1500° C.), though these temperatures are not always reached, some bauxite bricks being heated to only Cone 8 (1250° C.), which may be regarded as the minimum permissible temperature and a higher one is very desirable.

Articles made of crystalline or artificially prepared alumina, such as *alundum* pyrometer tubes and electric furnace cores, are preferably burned at about Cone 14 (1410° C.).

Magnesia bricks of the best quality are generally made of magnesia which has been fired at Cones 17–18 (1480°–1500° C.), whilst those containing a considerable proportion of iron oxide are burned at Cones 11–12 (1320°–1350° C.). Still higher temperatures would be preferable for calcining or " dead-burning " the magnesia as it is practically impossible to overheat it, but owing to the great cost of using very high temperatures the magnesia and the bricks are seldom heated higher than the above-named temperatures. At Eubœa, however, the Societé des Travaux Publics

et Communaux has stated that the magnesia bricks made by it are always fired at Cone 35 (1770° C.) in Mendheim gas-fired kilns, whilst in Austria some firms fire the bricks to Cones 26–30 (1580°–1670° C.).

Chromite bricks should preferably be burned at Cone 16 (1460° C.) or at a higher temperature.

Carbon bricks do not require such a high-burning temperature as some refractory bricks and very often they are finished at Cone 05*a*–1*a* (1000°–1100° C.), but it is desirable to heat them to Cone 10 (1300° C.), because when they are fired at too low a temperature they are rather weak.

Carbide bricks are burned at various temperatures according to the properties which are desired. Siloxicon bricks are usually burned at about Cone 14 (1410° C.), whilst carborundum bricks are burned at various temperatures up to Cone 35 (1770° C.). The higher the burning temperature, the more pronounced is the cellular crystalline structure of the bricks, this latter being highly desirable. The Carborundum Co., in one of its patents (1902), specifies that the bricks should be fired until this structure is developed.

Saggers are not usually burned to a very high temperature, but are generally placed in the same kiln as the ware which will later be fired in them, the new saggers being burned on top of those in use. When possible, it is much better to heat them in a separate kiln and to burn them to a higher temperature than that at which they are to be used, as this ensures maximum durability.

Glass-melting pots are seldom properly fired before use, but are generally baked or annealed at about Cone 05*a* (1000° C.) so as to make them just strong enough to be transported to the furnace in which they are to be used. It would appear to be better, though the cost would be great, to burn them at a high temperature before use, as this would result in a much stronger and more durable pot. Glass manufacturers contend, however, that the lightly burned pots withstand the sudden rise in temperature when they are placed in the furnace, better than those which have been more intensely heated in the course of manufacture, and as the pots eventually reach the temperature of the glass-melting furnace the importance of this contention must not be overlooked.

Retorts are generally burned at about Cone 12 (1350° C.) as specified by the Institution of Gas Engineers, but retorts of much better quality would be obtained if a temperature of Cone 14 (1410° C.) were reached. The firing temperature should, in any case, be higher than that at which the retorts are to be used so as to reduce the contraction, when in use, to a minimum.

Crucibles are not usually burned at a high temperature, but are merely " baked " at a bright-red heat which enables them to be handled easily. It is considered unnecessary to fire them at a greater temperature, as they attain this when in use. Whilst this practice is cheap, it is not really satisfactory, as the crucibles are not so strong as if they had been properly burned before use. Crucibles containing a large proportion of grog are generally burned at Cones 7–12 (1230°–1350° C.) before use, as their strength would be very low if they were merely baked at a lower temperature.

Plumbago or graphite crucibles are heated to Cones 018–010*a* (710°–900° C.). Table CXLIII shows the burning temperatures of various refractory materials :—

TABLE CXLIII.—*Firing Temperatures of Refractory Materials and Articles*

Material.	Finishing Temperature.	
	° C.	Seger Cone.
Bauxite bricks	1500	18
Chrome bricks	1450	16
Crucibles	1000	05*a*
Fireclay bricks	1250–1500	8–18
Glass-melting pots	1100	1*a*
Grog	1500	18
Lime	900–1200	010*a*–6*a*
Magnesia bricks	1500	18
Porcelain ware	1300–1500	10–18
Retorts	1500	18
Saggers	1350	12
Silica bricks	1200–1500	6*a*–18

From the foregoing pages it will be seen that in burning all articles made of ceramic materials there is formed a quantity of vitreous or glassy material, the first portion of which surrounds the more refractory grains and later portions gradually fill the interstices between them and also dissolve the grains so that, eventually, if the heating is sufficiently prolonged, at a suitable temperature, the whole of the material would form a molten liquid and all the reactions which could take place in order to produce a state of equilibrium at that temperature would be completed. As this would involve complete destruction of the article, the reactions which occur must be arrested at a point at which sufficient vitreous material has been formed to impart to the article (when cold) the desired properties of which the chief are usually the strength and porosity, though other properties dependent thereon, such as resistance to acids as well as other independent properties, may require to be considered in determining the finishing temperature and the duration (if any) of the soaking period. Thus, if colour is of great importance, as in some pottery and terra-cotta, the finishing temperature must be low and the proportion of vitreous material small ; if the strength of the product is to be the predominant property, the finishing temperature must be higher and the soaking period prolonged so as to produce a larger proportion of vitrified material ; whilst if complete impermeability, resistance to acids, hardness, or translucency, or any of these are to be predominant, the finishing temperature must usually be very high and the duration of the soaking very prolonged in order that the reactions which produce the fused vitreous material may proceed as far as possible without causing loss of shape in the product.

To anyone acquainted, even to a minor degree, with the nature of the reactions involved and the necessity of arresting them at precisely the right time, the firing of porcelain and some other forms of ceramic ware, under the conditions and with the restrictions imposed in commercial work, must be a continual source of wonder. Were we less accustomed to it we should find it difficult to believe that such complex reactions should be controlled so effectively, with such crude and imperfect means as are used regularly in the manufacture of earthenware, china-ware, and other pottery of the highest quality. In probably no other industries does the art of controlling chemical reactions, whose very nature is largely unknown, rise so high as in the firing of ceramic wares.

Effects of Withdrawing Heat

When the supply of heat to an oven or kiln containing ceramic articles (or to a furnace or other structure of which they form a part) ceases the articles gradually cool down. The heat will be lost slowly if the kiln or oven is tightly sealed, but it may be withdrawn rapidly by passing a sufficient quantity of cold air through the chamber. The latter will usually destroy the goods by causing them to crack and disintegrate, as most ceramic materials, when fired, are sensitive to sudden changes in temperature. To avoid damage, it is necessary to ascertain what are the best conditions for cooling. These naturally differ with the nature of the product, but, as a general rule, the more porous the material, the more rapidly can it be cooled with safety. Glass, or ware containing a large proportion of vitreous matter, on the contrary, must be cooled skilfully, and it is usually necessary with such materials to vary the rate of cooling at different temperatures; this variation or control of the cooling is known as *annealing*.

It is usually possible and desirable to allow the ware to cool rapidly from the finishing temperature to about 900° C., but below the latter temperature the cooling must usually be much slower, and even above it an excessive rate of cooling may be dangerous with large, thick pieces of highly vitrified ware.

Many fused and vitreous materials tend to crystallise if maintained too long at a temperature above 900° C., so that rapid cooling through the "crystallisation zone" is essential where a vitreous structure is desired as in glazes and in most ceramic ware.

Cooling the kilns improperly is a fruitful source of many defects, especially "crazing," "cracks," "dunts," and "feathering" or crystallisation, and great skill and care are needed to avoid them.

The few investigations which have been made on the effect of cooling ware at different rates during various stages of cooling show that there is scope for a very careful study of this subject. At present there is not sufficient information for any precise statement to be made on the various rates which should be adopted; they appear to differ with each class of ware.

Chemical Changes in Cooling.—The temperature at which cooling commences and the rate at which the cooling proceeds is very important, as it controls the conditions under which the reactions which eventually lead to the fusion of the material

are arrested. If the rate of cooling is very slow, the reactions will proceed much further than would be the case if it were rapid. Apart from this no chemical changes occur which would not take place during the soaking stage of firing (p. 550).

The **physical changes** which occur on cooling are chiefly those connected with the solidification of any fused matter present. This usually sets to an amorphous solid glass or slag, but if the cooling is very slow crystallisation may occur, the nature of the crystals produced depending on the composition of the molten material (see Chapter XI). The change of silica, magnesia, etc., from their high temperature forms to allotropic forms corresponding to lower temperatures also occurs if the rate of cooling permits it, but this is seldom the case.

The changes in specific gravity, volume, and conductivity are usually the reverse of those which occur in the firing, but they proceed at a far slower rate and, therefore, to a much smaller extent.

In most cases the strength of ceramic materials increases as the temperature falls and is much greater in the cold than when they are at a high temperature. This is due to the cold vitrified material forming a strong bond uniting the remaining particles firmly together, whereas when the materials are at a high temperature the vitrified material is in a soft or even in a fluid state and cannot resist so great a pressure as when it is cold and solid.

Effects of Excessive Heating

When any ceramic material or article is heated under such conditions that it loses its shape, swells undesirably, or undergoes any other changes which reduce its usefulness for the purposes for which it is intended, it is said to be *over-burned*. Over-burning is also said to occur when a material which should be highly porous becomes less so, even though it does not lose its shape. If an undesirable colour is produced as a result of excessive heating, the article or material is also said to be over-burned.

Over-heating may, therefore, be described as any result of heating which enables the reactions which lead to fusion to progress further than is desired in the particular case under consideration. Hence, what may be a sign of over-burning when a material is required for some purposes may indicate the opposite (under-burning) of the material for other purposes.

Over-heating may be due either to the material or article being raised to too high a temperature, to the heating being unduly prolonged or to the heating being repeated too frequently.

Distortion or **squatting** occurs when the amount of fused material present in a mass is sufficient to cause the latter to change its shape. The cause of this distortion is the mobility acquired by the solid particles in the presence of the molten material, whereby the mass as a whole cannot resist the pressure due to its own weight and, therefore, becomes reduced in height and increased in width until a shape is reached at which the whole mass remains in a state of equilibrium. If the temperature rises still further, or if the heating is prolonged at the critical temperature, more molten material will be formed and still further changes of shape will occur, until eventually

the whole mass becomes fluid. The increase in mobility may be due either to the material being heated to too high a temperature, to the heating being too prolonged or the pressure too great. The difference between the temperature at which squatting begins and that at which the whole mass is fused and becomes fluid is termed the *fusion range* (p. 524), whilst the refractoriness (defined on p. 525) is intermediate between the two extremes of this range.

As particles immersed in or floating on a fluid move more readily when pressure is applied to them, the amount of squatting is greater when a ceramic material is heated under pressure, or, alternatively, the change in shape occurs at a lower temperature because of the increased mobility of the solid particles when under pressure. Hence, the resistance to heat or refractoriness of a material is lower when it is under pressure or supports a load (p. 164), than when it is quite free.

The shape of a mass also affects the temperature at which squatting first appears, a tall mass changing its shape at a lower temperature than a short one, as the pressure on unit area in the lower part of the latter is much less. The shape of the mass before heating also determines that after squatting has commenced ; thus, Seger cones bend over (fig. 50) before becoming wholly liquid.

Boiling, or the conversion of a liquid into vapour or gas, will occur if the liquid is raised to a sufficiently high temperature without it undergoing decomposition. This change seldom occurs in ceramic materials as their boiling-points are usually unattainable in commercial furnaces. Glazes sometimes present the appearance of having been suddenly solidified whilst in a state of ebullition, but this is due to a wholly different cause and is quite distinct from true boiling, being caused by the partial escape of moisture or other gases from the ware after the glaze has been fused. A spurious boiling also occurs when clays rich in carbonaceous matter are heated too rapidly, the surface of the clay being sealed with fused material before the gases formed by the burning carbonaceous matter has escaped from the mass (p. 546).

The **volatilisation** of some of the constituents of ceramic materials may occur at very high temperatures. Thus, the alkalies and some of the silica in clay may be partially volatilised so that when clays are heated repeatedly at high temperatures they become slightly more refractory (see also p. 551).

Thus, Mellor [1] found that nearly 20 per cent. of the alkalies in an earthenware body were volatilised by overfiring it at 1400° C. Under reducing conditions, the loss is still greater as also in the presence of water vapour. Mellor [2] also found that a sagger lost 22 per cent. of its alkalies after firing it seven times at 1200° C.

The volatilisation of alkali from some glazes and the resultant dulling of the glaze is mentioned on p. 562.

Silica is appreciably volatile at high temperatures, especially in the presence of carbon, as the latter appears to reduce it to silicon which volatilises and is again oxidised and re-forms silica. This change of composition does not occur to any very great extent below 1750° C., but at higher temperatures quartz crystals, large enough to be readily seen with the naked eye may be completely volatilised in a reducing

[1] *Trans. Eng. Cer. Soc.*, **5**, 75 (1906).
[2] *Ibid.*, **6**, 130 (1906–7).

atmosphere. In the absence of carbon, however, silica does not appear volatile at any attainable temperature.

Effect of Prolonged Heating

The effect of a prolonged "soaking" during the firing of ceramic materials has been described on p. 550. A moderately long "soaking" is often beneficial, but if it is unduly prolonged, the effect may be deleterious instead of useful, as the production of an excessive amount of fused matter may endanger the stability of the mass or crystallisation may cause a decrease in strength and may render the material brittle or, as in the case of devitrification of silica glass, it may spoil the material for the purpose for which it is intended. R. Sosman found that devitrification occurs when fused silica is continuously heated at 200°–275° C. for a long period of time, on account of the α-β-inversion range (p. 329) which occurs at or near this temperature.

As a prolonged heating at a lower temperature has the same effect in producing fused material as a much shorter heating at a higher temperature, an excessively prolonged heating may cause distortion or squatting (p. 560). It may also cause excessive shrinkage in clay wares or excessive expansion in siliceous materials, if the finishing temperature during the burning of the ware was not sufficiently high, and these changes in volume may endanger the stability of the mass.

Swelling, bloating, and similar defects may occur as a result of prolonged heating at high temperatures, and if any fluxes are present which can combine with silica or bases, an increased amount of fused material may be produced, so that the effect of excessively prolonged heating is similar to that of heating the material to too high a temperature and so over-burning it (p. 560).

As volatilisation of part of the soda and potash may occur if the heating of the glaze is prolonged and this may lead to the glaze becoming dull instead of glossy, undue prolongation of the heating at the finishing temperature of glazes should be avoided.

Excessive heating of a molten glaze in contact with clay will usually enable reactions to occur between them with the result that an unfused product is formed. This destroys the glossy appearance of the glaze and so makes the ware defective. Such reactions are precisely the same as those which occur when a crude clay or pottery body is heated excessively, but the effect being confined more closely to the surface of the ware is more easily observed.

Prolonged heating at a sufficiently high temperature enables the reactions which lead to complete fusion to progress further than if the period of heating were shorter so that its general effect (that of over-burning) is the same as that when these reactions are not arrested at the proper time (p. 560).

Hence, prolonged heating, whether during the firing in the course of manufacture of the articles or whilst the articles are in use, may be either useful or harmful. If it forms part of the firing process it is generally useful as it increases the strength and resistance to acids and abrasion and reduces the porosity (p. 69), but if the prolonged heating occurs when the articles are in use, its general effect is harmful, as it tends to increase the amount of fused matter present. For this reason, ceramic materials

which require to be heated to high temperatures during long periods should be of a highly refractory nature, or they will eventually collapse through squatting or analogous distortion (p. 560).

Effect of Repeated Heating

When ceramic materials are repeatedly heated and cooled the effect is similar in many respects to that of prolonged heating (p. 562), the same kind of changes taking place in both cases.

The effects of repeated heating and cooling also differ according as the treatment is (*a*) at a rapid rate, and (*b*) at a slow rate.

The effect of rapid heating and cooling when repeated many times is discussed in the section on *The Effect of Sudden Changes of Temperature* (p. 581).

The chief materials which are subjected to repeated heating and cooling are the walls of some kilns and furnaces, saggers, glass-melting pots, continuous retorts, crucibles, etc.

The effect of repeatedly heating *saggers* to temperatures between Cones 8 and 16 (1250°–1460° C.) is to reduce the strength on account of the strains set up in the material and also increase the tendency to crystallisation. For this reason, most English saggers can only be used fourteen to fifteen times, though in some works on the Continent where saggers of better quality are employed, they will stand fifty or more heatings. The difference is largely due to the care taken in the selection and preparation of the materials of which the saggers are made.

Crucibles, when repeatedly heated, become hard and vitreous as a result of the action of the contents upon the crucible. The resistance of the crucibles to sudden changes of temperature is correspondingly decreased so that after a time crucibles " perish " and can no longer be used.

When *fused silica* is repeatedly heated at about 1200° C. it shrinks and devitrifies forming tridymite or cristobalite, especially in the presence of basic or alkaline dust or ash.

In all these instances, the effect of repeated heating is to permit the various reactions which lead to ultimate fusion to make further progress to completion and to overcome the arrest of these reactions which occurs when the article or material is allowed to cool for the first time. Repeated heating at a moderately high temperature also facilitates the production of a state of equilibrium by the formation of crystals from a molten or vitreous mass, and, consequently, effects partial devitrification.

Effects of Heat on the Volume of Ceramic Materials

The changes in volume which occur when ceramic materials are heated or cooled may be divided into two groups :

(*a*) Permanent expansion or contraction.
(*b*) Reversible expansion or contraction.

The permanent expansion or contraction is due to chemical or physical changes in the materials, and, as is characteristic of them, such changes take an appreciable time to occur, whilst a reversible expansion is common to all materials and is almost instantaneous in its occurrence so that it cannot be arrested, however quickly the substance may be heated or cooled. Permanent changes in volume can, on the contrary, be arrested by rapid heating or rapid cooling. The difference between these two kinds of volume change is discussed further on p. 520.

The effect of heat on the total volume of a material may differ greatly from that on the individual particles composing the mass as a whole. Thus, in a mixture of silica and clay, the individual grains of silica will expand and those of the clay will shrink when heated and the result may be that the total volume of the brick or other article made of such a mixture may be unaffected. Semi-silica bricks of this character are largely used where constancy in the volume of a structure, such as a retort or coke oven, is important.

In consequence of the difference between the behaviour of the mass or article as a whole, and that of its constituent parts, care must be taken in investigating or studying the effects of expansion and contraction to distinguish clearly between these changes.

Permanent Volume-Changes

Permanent changes in volume differ with the materials in which they occur. The chief change which occurs when ceramic materials are made into various articles and fired is the contraction or shrinkage which occurs when they are heated. Some materials, such as suitable mixtures of clay and silica, are practically constant in volume, whilst others, such as silica, expand when heated and do not regain their original volume on cooling. The extent to which these permanent changes in volume are completed in any given material depends chiefly upon the temperature to which it is heated, so that when firing ceramic materials which are required to have a constant volume when in use, they should be finished at such a temperature as will ensure these permanent changes taking place to the fullest extent.

The principal causes of the permanent changes in volume are :—

(*a*) The nature and composition of the material.
(*b*) Its previous treatment (if any).
(*c*) The sizes and grading of the grains.
(*d*) The pressure applied in shaping the articles.
(*e*) The proportion of water used in mixing the materials.
(*f*) The porosity of the material.
(*g*) The temperature at which the material has been fired or reheated.

From the above it will be seen that the permanent changes in volume may be divided into two groups :

(i) Changes which are dependent upon the inherent qualities of the materials.
(ii) Changes which are dependent on the method of manufacture.

The changes in the first group have been described in the previous chapters on *Chemical Constitution*, *Specific Gravity*, *Chemical Reactions*, etc., and are chiefly due to—(*a*) decomposition and the removal of some constituent which causes a reduction in volume, as in the case of clay; (*b*) to the formation of other allotropic forms of the same material which cause a change in the specific gravity and, consequently, either an expansion or contraction; or (*c*) a chemical reaction which produces a new material of greater specific gravity and with consequent volume change.

The physical causes of change in volume, such as texture, porosity, etc., are considered in the respective chapters dealing with these subjects.

Whilst it is very desirable it is not always possible to complete the various changes in volume which occur during the firing of ceramic materials, so that a compromise must usually be made, and—where it is important—the maximum permissible permanent expansion or contraction in use should be specified. This is particularly the case with refractory materials, as it is in these that after-contraction or expansion is most harmful.

Clays, when properly burned, shrink permanently to a varying extent, depending on their composition. This contraction or shrinkage takes place in two stages: (*a*) shrinkage during drying, and (*b*) shrinkage during burning. The shrinkage in drying is due to the removal of water from the surfaces of the grains and has been described in Chapter VII. The kiln- or fire-shrinkage of clays is due to their decomposition, with the consequent loss of water (p. 350) and the gradual drawing together of the resultant anhydrous grains. In the case of an earthenware or porcelain, the shrinkage due to the loss of water is partly counterbalanced by an expansion due to the fusion of crystalline silicates and the transformation of flint and quartz into the low specific gravity forms of silica which have a greater volume than the original materials.

The amount of shrinkage is to some extent dependent on the fineness of the particles, fine-grained materials shrinking more than coarse-grained ones.

There appears to be little or no fire-shrinkage between 600° C. and 900° C., but above 900° C. the shrinkage increases considerably in amount up to 1100° C. It thus appears that during the burning of the carbonaceous matter scarcely any shrinkage takes place, so that the temperature may safely be raised fairly rapidly between 600° and 900° C. if little carbonaceous matter is present. Shrinkage continues up to the highest temperature at which the clayware is fired and would still continue, if the heating were prolonged, up to the point at which fusion occurs, unless the conditions are such as to cause bloating, when an expansion would result. Consequently, clays will always shrink in use if they are then heated to a temperature higher than that attained in the firing. This is very important in connection with refractory clays, which should be fired at a sufficiently high temperature to prevent an excessive contraction in use.

Mellor has shown that if it is assumed that the change of contraction during the firing is proportional to the square of the contraction which has yet to take place, the effect of repeated heating at 1130°–1150° C. (Cone 2*a*–4*a*) approximately

follows the law for bimolecular reactions and the contraction may be calculated as follows :—

$$x = \frac{a^2kt}{1 + akt},$$

where x is the contraction after any number of firings t, a is the maximum contraction after an indefinite number of firings, and k is a constant depending on the nature of the material. He found that fireclay bricks contracted more in a reducing atmosphere than in an oxidising one, as shown in the following figures :—

TABLE CXLIV.—*Contraction of Firebricks*

Material.	Burning Temperature, Cone.	Contraction Percentage.		Expansion.	
		Oxidising Atmosphere.	Reducing Atmosphere.	Oxidising Atmosphere.	Reducing Atmosphere.
Fireclay bricks .	14	..	..	0·21	nil.
,, .	14	..	0·33	..	..
,, .	14	1·12	1·27	..	..

The increased contraction is probably due to the greater fluxing effect of the iron in a reducing atmosphere.

The specification of the Institution of Gas Engineers directs that first-class fireclay bricks shall not contract more than 1 per cent. when reheated for two hours at Cone 14, whilst second-class fireclay bricks shall not contract more than 1·25 per cent., the test-pieces in each case being $4\frac{1}{2}$ inches square.

A noteworthy expansion or contraction is very harmful in the case of retorts, and should specially be avoided by using suitable materials and burning them at a sufficiently high temperature. To avoid troubles which would otherwise occur, the Institution of Gas Engineers specifies that a test-piece $4\frac{1}{2}$ inches square, cut from a clay retort, when heated at 1350° C. (Cone 12) for two hours should not contract more than 1 per cent. in length. It is also important that the reversible expansion or contraction of retorts when in use should also be as low as possible, as it is the changes in volume of the retort whilst it is hot which are one of the chief causes of its disintegration. This is avoided in some bricks, retorts, etc., by using a siliceous clay in such proportions that the expansion of the silica is neutralised by the contraction of the clay, and, consequently, the material is almost constant in volume.

G. A. Loomis has found that firebricks which can retain their shape when heated to a temperature of 1350° C., under a pressure of 40 lb. per square inch, seldom show

more than very slight permanent changes in volume when they are heated to a temperature of 1425° C. If the porosity of a ceramic material decreases more than 5 per cent. and the change on firing exceeds 3 per cent. by volume, or 1 per cent. of the original length of the test-piece, the latter will not withstand the load or pressure mentioned. He considers that the porosity and volume tests form a useful means of checking the ability of fireclay bricks to withstand the load test (see also p. 166).

When an appreciable proportion of fused matter is produced—either as a result of the very high temperature attained or of the presence of fluxes—its effect on the shrinkage is very marked. For this reason, semi-vitrified and vitrified clay wares shrink more than articles made of refractory clays which do not contain much flux and so are only slightly vitrified. As the fusion proceeds the material, as a whole, shrinks rapidly at first and more slowly later, the amount and rate of shrinkage depending largely on the nature of the flux, soda, potash, and whiting being the most active in this respect. The effect of lime compounds on an earthenware body is shown in Table CXLV, due to H. E. Ashley.[1]

TABLE CXLV.—*Effect of Lime Compounds on Earthenware*

Nature of Flux.	Flux, per cent.	Linear Shrinkage, per cent.
Fluorspar . .	. .	10·5
,, . .	0·1	11·1
,, . .	0·3	11·1
,, . .	1·0	10·8
,, . .	3·0	11·4
Whiting . . .	0·13	11·1
,, . . .	0·4	11·3
,, . . .	1·0	11·8
,, . . .	3·0	12·7

As the shrinkage is due to the combination of the flux with the clay, resulting in the production of a molten fluid, any materials which will produce such a fluid will cause the ware to shrink during the firing. Hence, it is scarcely necessary to describe the action of any fluxes in detail, though the following observations may be mentioned :—

H. Hope [2] has observed that barium and zinc oxide tend to increase the firing shrinkage of china bodies. Various investigators have noted that mica slightly increases the kiln shrinkage of clay, but if a large proportion of muscovite is present

[1] *Trans. Amer. Cer. Soc.*, **8**, 148 (1906).
[2] *Ibid.*, **11**, 522 (1909).

a slight expansion may occur at about Cone 10 (1300° C.). Magnesia and magnesite also increase the shrinkage of clays and also the vitrification range.

Silica bricks expand considerably during the burning, in course of manufacture, on account of the conversion of quartz to tridymite or cristobalite (p. 329), which involves a volume-expansion of more than 20 per cent. or at least $\frac{7}{8}$ inch per linear foot. The complete conversion is never effected in commercial practice during the firing of the bricks, but a slow and constant expansion continues whilst the bricks are in use at high temperatures, so that if the bricks are to be as constant in volume as possible when in use, they must be heated sufficiently during the first firing to effect as much as possible of the total expansion. Bricks which have not been heated sufficiently during the firing may fail—as the result of continued expansion—when in use.

The Institution of Gas Engineers (1912) in its standard specification requires that silica bricks when heated for two hours at Cone 14 (1410° C.) shall not show more than 0·75 per cent. linear expansion or contraction, the test being made on a sample $4\frac{1}{2}$ inches square.

More recently, K. Endell,[1] after examining many bricks and numerous specifications, has suggested that silica bricks should not expand more than 2 per cent. linear if they are heated to 1600° C. in one and a half hours, and maintained at that temperature for a further period of half an hour. The change in volume, in burning silica bricks at various temperatures, observed by R. M. Howe and W. R. Kerr,[2] is shown in Table CXLVI, which clearly indicates the importance of a high-finishing temperature for silica bricks.

TABLE CXLVI.—*Average Residual Expansion on Burning Silica Bricks to Various Temperatures*

Burning Temperature.		Residual Expansion.
Cone.	° C.	per cent.
11	1320	4·2
14–15	1410–1435	2·0
16–17	1460–1480	1·3
17	1480	0·8
18	1500	0·4
19	1520	0·2

Table CXLVII, due to K. Endell,[3] shows a comparison between the after-expansions (on re-heating) of silica bricks made by different firms.

[1] *J. Amer. Cer. Soc.*, **5**, 209 (1922).
[2] *Loc. cit.*, p. 217.
[3] *Ibid.*, **5**, 216–17 (1922).

TABLE CXLVII.—*After-Expansion of Silica Bricks*

Type of Bricks.	Linear Expansion after Heating ½ hr. at 1600° C., per cent.	Unaltered Quartz, per cent.
German—		
Average of 8 basic open-hearth furnace bricks	3·7	28
Average of 3 coke-oven bricks	4·7	32
Glass furnace bricks	4·0	40
Average of 4 bricks made by German steel works for their own use	0·8	13
American—		
Medina Quartzite (Star)	0·5	14
English—		
Ganister brick	3·5	22
Swedish—		
Quartzite brick	2·8	16

According to J. W. Mellor,[1] silica bricks expand less in a reducing atmosphere than in an oxidising one, as shown in Table CXLVIII; this is probably due to the greater fluxing effect of the iron compounds when heated in an oxidising atmosphere, with the production of ferrous silicates which fill the interstices of the bricks.

TABLE CXLVIII.—*Expansion of Silica Bricks* (*Mellor*).

Temperature of Burning.	Expansion per cent.	
	Oxidising Atmosphere.	Reducing Atmosphere.
Cone 12	0·20	0·13
,,	0·13	0·12
Cone 14	0·58	0·48
,, [2]	contracted 0·44	contracted 0·77

Bauxite bricks shrink greatly when fired during their course of manufacture even though the raw material has been calcined at a very high temperature. It is, therefore, important that bauxite bricks should be properly fired during manufacture, or they may shrink excessively when in use. The chief changes which accompany and probably cause the shrinkage are the decomposition of the bauxite with evolution of combined water, together with a later change due to the polymerisation of the resulting alumina. The finest grained bauxite bricks usually shrink less in use than those made from coarser materials.

[1] *Trans. Eng. Cer. Soc.*, **16**, 268 (1916–17). [2] This brick was an unusually fine-grained one.

Table CXLIX, due to Howe and Ferguson,[1] shows the shrinkage of various aluminous materials (diaspore, bauxite, and gibbsite).

TABLE CXLIX.—*Shrinkage of Aluminous Materials*

	A.	B.	C.	D.	E.	F.	G.
Percentage of alumina . .	56·31	52·48	67·21	60·89	60·66	61·98	73·70
Percentage of water . .	28·08	17·90	13·74	13·41	9·88	14·98	14·24
Shrinkage on drying . .	8·30	5·50	11·60	5·80	8·40	3·70	10·20
Burning shrinkage at Cone 3 .	18·00	12·70	8·20	12·20	12·20	16·70	1·30
Burning shrinkage at Cone 18 .	42·60	30·80	29·90	16·30	55·20	38·20	16·30

Fused alumina shows no permanent changes in volume when in use, as the high temperature required for its fusion enables all the reactions which result in a change in volume to be completed prior to its use.

Sand-bauxite bricks (which are made of a mixture of bauxite and crushed quartz) shrink less in use than ordinary bauxite bricks as the expansion of the quartz neutralises some of the contraction of the bauxite. Unfortunately, the refractoriness of the latter is considerably reduced by the addition of sand.

Magnesia bricks, made from dead-burned magnesia, should not shrink in use, but if the material of which they are made has not been fully dead-burned, shrinkage will continue whilst the bricks are in use until the whole of the magnesia has been converted into periclase.

Magnesia bricks of the best quality should not shrink more than 5 per cent. linear or 15 per cent. by volume when in use and if sufficient care is taken a much smaller percentage contraction in use will be experienced.

Other refractory wares, such as bricks, crucibles, etc., made of carbon, carbide, chromite, zirconia, etc., contract very little during the firing process and have a constant volume when in use. The kiln-contraction during manufacture is almost wholly due to the changes in volume of the bond. Such bricks, if properly made, show practically no after-contraction or expansion when in use, and are, therefore, very valuable as refractory materials.

REVERSIBLE VOLUME-CHANGES

Reversible changes in volume are those which occur when a material is heated and cease—with restoration of the original volume—when the material is cooled to its original temperature. Reversible changes are measured by the coefficient of expansion, which varies with different materials according to the

(*a*) Chemical composition.
(*b*) Texture.
(*c*) Temperature of the material.

[1] *J. Amer. Cer. Soc.*, **6**, 496 (1923).

Clays.—Kaolin and bauxitic fireclays have, after calcination, according to Houldsworth and Cobb,[1] a regular reversible expansion which does not vary much with the temperature of calcination.

They found that fireclays calcined at Cones 14–20 have a regular reversible expansion similar to kaolin as the quartz is destroyed by interaction with the fluxes present. The regular expansion is most readily attained with fine-grained and rather fusible materials, whilst it is retarded in the presence of a large amount of quartz.

Fireclays and glass-pot mixtures calcined at Cones 06–9 show a large expansion on heating between 500° and 600° C., according to Houldsworth and Cobb, on account of the quartz present and on cooling the contraction is larger than the corresponding expansion. The expansion between 100° and 250° C. after calcination at Cone 9 also exceeds the average.

Table CL shows the coefficient of expansion of various kinds of clays after calcination at various temperatures.

TABLE CL.—*Coefficient of Expansion of Clays* (*Houldsworth and Cobb*), *coeff. of Exp.* $\times 10^{-8}$

Substance.	Temperature Range, ° C.	Temperature of Firing prior to Test.			
		Cone 06.	Cone 9.	Cone 14.	Cone 20.
Kaolin . .	100–250	..	764	578	..
,, . .	15–1000*	402	531	477	441
Farnley fireclay .	100–250	..	1023	875	..
,, ,, .	15–500	481	769	676	..
,, ,, .	500–600	1331	1275	1075	..
,, ,, .	600–1000*	217	183	250	..
,, ,, .	15–1000*	491	583	540	305
Ball clay . .	15–500	542	..	..	..
,, . .	500–600	980	..	..	..
,, . .	600–900	431	..	..	..
,, . .	15–1000*	554	575	436	..
Ayrshire Bauxitic clay.	100–250	..	726	652	..
	15–1000*	480	605	561	418
Glasgow fireclay .	100–250	..	986	801	..
,, ,, .	15–500	401	745	542	..
,, ,,	500–600	1276	1220	886	..
,, ,,	600–1000*	279	294	364	..
,, ,,	15–1000*	457	611	554	395

[1] *J. Soc. Glass. Tech.*, **5**, 16 (1921).

The effect of porosity on the coefficient of expansion of fireclay is shown in Table CLI due to Houldsworth and Cobb.[1]

TABLE CLI.—*Effect of Porosity on Coefficient of Expansion of Fireclay*

Porosity.	Temperature of Calcination.	Range, ° C.	Coefficient of Expansion $\times 10^{-6}$.
28·7	Cone 9	15–500	769
		500–600	1275
		600–1000	183
		15–1000	583
44·6	,,	15–500	602
		500–600	1053
		600–1000	281
		15–1000	517
50·2	,,	15–500	550
		500–600	997
		600–1000	295
		15–1000	491
31·7	Cone 06	15–500	481
		500–600	1331
		600–1000	204
		15–1000	455
47·7	,,	15–500	441
		500–600	1220
		600–1000	211
		15–1000	426
62·7	,,	15–500	406
		500–600	1203
		600–1000	195
		15–1000	401

It will be seen that up to 50 per cent. an increase of porosity causes an appreciable diminution in the coefficient of expansion, but over 50 per cent. the change is comparatively small.

The average temporary expansion of a well-burned firebrick when heated to 1300° C. is about 0·000006 per 1° C.

The coefficient of other non-vitrified claywares is similar to that of firebricks. Mellor [2] found the coefficient of expansion of various kinds of tiles to be as follows :—

[1] *Loc. cit.*, p. 571.

[2] *Trans. Eng. Cer. Soc.*, **5**, 159 (1905–6).

TABLE CLII.—*Coefficient of Expansion of Tiles*

Material.	Range of Temperature.	Coefficient of Expansion.
Soft burned clay floor tiles . . .	15–100° C.	$71{\cdot}4\times10^{-7}$
Properly burned clay floor tiles . .	,,	$70{\cdot}3\times10^{-7}$
Hard burned clay floor tiles . .	,,	69×10^{-7}

The average is 0·000007 per 1° C.

Boeck [1] found the coefficient of expansion of a ball clay at different temperatures to be as follows :—

TABLE CLIII.—*Coefficient of Expansion of Ball Clay*

Temperature Range.	A.	B.
24–100° C.	1316×10^{-8}	1380×10^{-8}
100–200° C.	1710×10^{-8}	1610×10^{-8}
200–900° C.	..	567×10^{-8}
200–700° C.	558×10^{-8}	580×10^{-8}

Vitrified Claywares.—The coefficient of expansion of vitrified claywares varies considerably according to their nature and the extent of vitrification, but it is generally less than that of non-vitrified claywares.

Much work has been done on the coefficient of expansion of *porcelains* and much data has been compiled as to the effect of different factors upon it. The following information is a brief summary of what has been done.

Chemical composition has an important influence on the reversible changes in volume, as the proportions of the various materials present, in conjunction with the firing, determines the structure of the ware. Porcelain consists essentially of three constituents : (*a*) felspar, (*b*) clay, and (*c*) flint.

Felspar decreases the coefficient of expansion of porcelain. The effect of increasing the proportion of felspar in whiteware bodies, whilst keeping the proportion of flint constant is stated by Purdy and Potts [2] to be :—

With 30 *per cent. of Flint.*—The coefficient decreases from 0·0000065 with 1 felspar and 9 clay to 0·000004 with 4·5 felspar and 5·5 clay ; it increases rapidly with equal parts of felspar and clay and then slowly to 7 parts felspar and 3 parts clay at which the coefficient of expansion is 0·000007.

[1] *Loc. cit.*, p. 521. [2] *Trans. Amer. Cer. Soc.*, **13**, 431 (1911).

With 40 per cent. of Flint.—As the felspar increases to a ratio of 4·5 felspar : 5·5 clay the coefficient decreases gradually and then rises rapidly.

It will be seen that when the flint is constant between 30 and 40 per cent. the felspar decreases the coefficient of expansion as it increases up to 4·5 parts of felspar and 5·5 parts of clay, but that more felspar causes an increase in the coefficient.

When the *clay-content* is constant the effect of felspar is as follows :—

Clay. per cent.	Behaviour.
25	The coefficient of expansion falls with a felspar : flint ratio falling from 2 : 8 to 3·5 : 6·5 and rises again with ratios up to 6 : 4.
35	The coefficient falls from 1·5 : 8·5 to 3 : 7 is constant from 4 : 6, it falls slightly to 4·5 : 5·5 and rises to 5 : 5, after which it remains constant to 6 : 4.
45	The coefficient falls from 2 : 8 to 5 : 5 and then rises rapidly.
55	The coefficient is fairly constant from 2 : 8 to 4 : 6 and then falls to 5·5 : 4·5 and rises to 6 : 4.
60	The coefficient falls from 3·5 : 7·5 to 6 : 4 and then rises gradually.

These results show that there is a critical relation between the proportion of flint and felspar with any constant content of clay and that either more or less felspar than this critical amount decreases the coefficient of expansion. Similarly, an increase of felspar at the expense of flint in a mixture with a constant flint : clay ratio decreases the coefficient of expansion. As the percentage of clay is increased, more felspar and less flint is required to give a minimum coefficient of expansion.

According to Bleininger and Riddle,[1] the thermal expansion of beryllium porcelain is lower than that of felspathic bodies (Table CLIV).

TABLE CLIV.—*Thermal Expansion of Beryllium Porcelain*

Temperature Range, ° C.	Thermal Expansion.	Temperature Range, ° C.	Thermal Expansion.
26–200	$1{\cdot}63\times10^{-6}$	400–520	$3{\cdot}6\times10^{-6}$
200–400	$2{\cdot}95\times10^{-6}$	26–400	$2{\cdot}33\times10^{-6}$

Clay, according to Seger,[2] decreases the coefficient of expansion in porcelain, but Purdy and Potts[3] found this is only true when the total amount of clay present exceeds

[1] *J. Amer. Cer. Soc.*, **2**, 564 (1919).
[2] *Collected Writings*, **2**, 576.
[3] *Loc. cit.*, p. 573.

55 per cent. They found, contrary to Seger, that in a mixture containing less than 45 per cent. of flint, the addition of clay slightly increases the coefficient of expansion. Clay added at the expense of felspar, the percentage of flint being kept constant, also increases the coefficient of expansion. Purdy and Potts, therefore, conclude contrary to Seger, that, within the range of composition of useful porcelains, the addition of clay increases the coefficient of expansion.

Flint—added to the extent of 5 per cent. when the ratio of felspar : clay is kept constant—increases the coefficient of expansion from 0·000041–0·000052. The addition of a further 5 per cent. causes another increase in the coefficient of expansion, but the addition of a third 5 per cent. results in a slight decrease. A porcelain body containing 45–60 per cent. of flint has a large coefficient of expansion. In porcelain bodies with a felspar : clay ratio of 1 : 4, the coefficient increases when 25–35 per cent. of flint is present, then decreases to 45 per cent. and from that proportion increases to 65 per cent. In a mixture with a 1 : 1 felspar : clay ratio, the addition of 20–50 per cent. of flint causes an irregular decrease and the addition of 50–60 per cent. causes an increase in the coefficient of expansion. With a felspar : clay ratio of 3 : 7, the coefficient of expansion increases rapidly with the addition of 15–28 per cent. of flint, remains fairly constant with 28–45 per cent. of flint and then increases with 45–70 per cent. of flint.

Purdy and Potts also found, contrary to Seger, that within the range of composition which produces good porcelain, the addition of flint slightly decreases the coefficient of expansion and that the hard porcelain body with the lowest coefficient of expansion consists of 30 per cent. each of flint and felspar and 40 per cent. of clay.

A. S. Watts [1] has published the following information respecting the influence of the chemical composition upon the coefficient of expansion of European porcelain :—

(*a*) The addition of flint at the expense of felspar or kaolin increases the coefficient of expansion.

(*b*) Felspar and clay are interchangeable without any appreciable effect on the coefficient of expansion.

(*c*) The addition of ball clay at the expense of kaolin slightly increases the coefficient of expansion, whilst the substitution of English china clay for Zettlitz kaolin produces a marked increase in the coefficient of expansion.

(*d*) Finely-ground flint, added at the expense of the quartz sand occurring in kaolin, increases the coefficient of expansion.

(*e*) Calcined kaolin and flint are interchangeable without any great variation in the coefficient of expansion.

The coefficients of expansion of various porcelains at ordinary or comparatively low temperatures is shown in Table CLV.

[1] *Trans. Amer. Cer. Soc.*, **13**, 406 (1911).

[Table CLV.

TABLE CLV.—*Coefficient of Expansion of Porcelain*

Porcelain.	Temperature Range.	Coefficient of Expansion.		Authority.
		Linear.	Cubical.	
Bayeux . . .	0° C.	0·000002522	..	Tutton.
,, . . .	..	0·000005500	0·000016–0·000017	Deville and Troost.
Meissen . . .	0°–100° C.	0·000002690	..	Weinhold.
Berlin . . .	23°–200° C.	0·000003430	..	Rieke.
,, . . .	16°–191° C.	0·000001770	..	F. Henning.
..	..	0·000004000	..	Holborn and Wien.
Rosenthal laboratory porcelain.	..	352×10^{-8}	..	Singer and Rosenthal.
Seger porcelain (6833)	20°–100° C.	380×10^{-8}	..	,,

The coefficients of expansion of stoneware (p. 577), Marquardts' porcelain, magnesic porcelain, and ordinary glass (p. 581) are greater than the figures given above.

It has been found that the porcelains which have the greatest coefficient of expansion are those which are lowest in fluxes or which are least vitrified.

Texture appears to have an important influence on the coefficient of expansion, though little experimental work has been done to determine its limitations. It has, however, been found that, when other conditions are constant, porcelains fired at a very high temperature, or otherwise thoroughly vitrified, have a lower thermal expansion than others, on account of the increased vitrification, though Purdy [1] failed to find any definite relationship between the total porosity and the coefficient of expansion of various porcelains.

Temperature has a great influence on the coefficient of expansion of porcelains. According to Purdy, the graph representing the expansion of porcelain bodies containing 30 or more per cent. of flint at temperatures below 500° C. forms almost a straight line. At 500°–600° C., the rate of expansion increases, but above 600° C. it decreases. The higher the proportion of flint in the ware, the more pronounced are the changes in the rate of expansion. When less than 30 per cent. of flint is present the rate of expansion only changes slightly between 500° and 600° C.

Table CLVI shows the effect of temperature on the coefficients of expansion of various porcelains.

[1] *Trans. Amer. Cer. Soc.*, **15**, 499 (1913)

TABLE CLVI.—*Coefficient of Expansion of Porcelain at Various Temperatures*

Porcelain.	Temperature Range, ° C.	Coefficient of Linear Expansion.	Authority.
Bayeux . . .	0	0·000002522	Tutton.
,, . . .	50	0·000003265	,,
,, . . .	100	0·000004008	,,
,, . . .	120	0·000004305	,,
Berlin . . .	23–200	0·000003430	Rieke.
,, . . .	23–400	0·000003530	,,
,, . . .	23–600	0·000003550	,,
,, . . .	23–700	0·000003560	,,
Berlin . . .	191–16	0·000001770	F. Henning.
,, . . .	16–250	0·000003360	,,
,, . . .	16–500	0·000003640	,,
,, . . .	16–1000	0·000004340	,,

A. S. Watts [1] obtained some very irregular results for the coefficient of expansion of porcelain at different temperatures as shown in Table CLVII, but with most porcelains a fairly regular increase is obtained.

TABLE CLVII.—*Coefficient of Expansion of Porcelain at Various Temperatures*

Temperature, ° C.	Coefficient of Expansion.	Temperature, ° C.	Coefficient of Expansion.
16	0·000005357	139	0·000004650
55	0·000006127	196	0·000004860
72	0·000005738	243	0·000005350
102	0·000005416		

According to R. Rieke,[2] a sample of stoneware containing about 25 per cent. of flint and fired at Cone 7 (1230° C.) had the following coefficients of expansion at the temperatures stated :—

TABLE CLVIII.—*Coefficient of Expansion of Stoneware*

Temperature, ° C.	Coefficient of Expansion.	Temperature, ° C.	Coefficient of Expansion.
15–200	130×10^{-7}	500–600	140×10^{-7}
200–500	70×10^{-7}	600–1000	50×10^{-7}

[1] *Trans. Amer. Cer. Soc.*, **9**, 86 (1909).

[2] *Ber. der Tech. Wiss. Abt. des Verb. Keram. Gewerke*, **5**, 8–15 (1919).

As shown in the table, Rieke's results do not show so regular an expansion as most porcelains; the difference is probably due to the fact that stoneware is intermediate in structure between an unvitrified, porous structure and a true porcelain or glass, and that the coefficient of expansion of such stoneware must depend on the relative proportion of each of these forms of structure.

Various formulæ have been devised for calculating the expansion of porcelain at different temperatures, amongst which are shown in Table CLIX, compiled by Purdy and Potts [1]:—

TABLE CLIX.—*Formulæ for the Expansion of Porcelain*

Porcelain.	Temperature Range, ° C.	Formula.	Authority.
Bayeux . .	. .	$Lt=L_0(1+at)$	Deville and Troost.
Electric insulator .	19–243	,,	Watts.
Berlin .	0–1500	,,	Holborn and Wein.
Bayeux .	0–830	$Lt=L_0(1+(3425t+1{\cdot}07t^2)10^{-9})$	Bedford.
,, .	0–83	$Lt=L_0(1+(2824t+6{\cdot}17t^2)10^{-9})$	Chappins.
,, .	10–120	$Lt=L_0(1+(2522t+7{\cdot}43t^2)10^{-9})$	Tutton.
Berlin .	250–625	$Lt=L_0(1+(2945t+1{\cdot}125t^2)10^{-9})$	Holborn and Day.

(Lt=coefficient at temperature t° C., L_0=coefficient at 0° C., and a is a constant.)

T. G. Bedford [2] states that the length of a sample of porcelain at any temperature may be found from the formula

$$l(1+34{\cdot}25\times10^{-7}t+10{\cdot}7\times10^{-10}t^2),$$

where l is the length at 0° C. and t is the desired temperature in ° C., the curve expressing the elongation being of the form $(ax^2+bx+1)K=y$, but Deville and Troost, as well as Holborn and Wien, consider that the curve takes the form $(ax+1)K=y$.

Glazes must have a coefficient of expansion very similar to that of the body to which they are attached or they will either "craze" or "peel" according as the expansion is greater or less than that of the body. Some authorities, however, do not attach so much importance to the coefficient of expansion as to other properties, such as the toughness or tensile strength of the glaze. Thus, F. Singer and E. Rosenthal [3] consider that the fitting of the glaze depends on the coefficient of expansion, elasticity, tenacity, pliability, and resistance to stress and strain of the two components, and Purdy and Potts [1] have suggested that the coefficient of expansion of glazes and bodies cannot have the great importance often attached to it in connection with crazing as they have found, as also have others, that some glazes behave equally

[1] *Loc. cit.*, p. 573.
[2] *Brit. Assoc.*, 1899.
[3] *Ber. deut. Keram. Ges.*, **1**, 3 (1920); *Sprech.*, **54**, 250 (1921).

well on bodies high in felspar with a vesicular structure as on bodies high in flint which are not vitrified. Such behaviour would be explained if the glazes had sufficient tensile strength to withstand the strains set up in them during the cooling of the ware.

According to R. Rieke,[1] the coefficient of expansion of porcelain glazes varies from 27×10^{-7} to 42×10^{-7}. The latter figure is very similar to the coefficient of expansion of porcelain, which at 700° C. is about 35×10^{-7}.

According to the same authority, white-ware glazes have a coefficient of expansion between 57×10^{-7} and 96×10^{-7}.

Table CLX shows the capacity of various oxides for increasing the coefficient of expansion of enamels; the results are not always quite accurate, but give some idea as to the effect of various fluxes on the expansion.

TABLE CLX.—*Relative effect of Oxides on the Expansion of Glazes*

Oxide.	Relative Activity.	Oxide.	Relative Activity.
Soda . . .	10	Lead oxide .	3·0
Potash . .	8·5	Barium oxide .	3·0
Alumina . .	5·0	Silica . .	0·8
Lime . . .	5·0	Boric oxide . .	0·1

Siliceous materials vary in their reversible expansion according to their origin. Houldsworth and Cobb[2] give the following figures for the coefficient of expansion of various siliceous materials in the raw state :—

TABLE CLXI.—*Coefficient of Expansion of Raw Siliceous Materials*

Material.	Temperature Range.	Coefficient of Expansion $\times 10^{-7}$.
Meanwood Ganister (no bond) . .	15–1000	180
,, ,, (lime bond) . .	,,	136
Welsh quartzite (lime bond) . . .	,,	136
Flint (lime bond)	,,	174
Precipitated silica with 5 per cent. soda	15–700	132

They found the average reversible thermal expansion of manufactured silica bricks between 150° C. and 1000° C. was 1·1–1·3 per cent.

[1] *Loc. cit.*, p. 577.

[2] *Trans. Eng. Cer. Soc.*, **21**, III, 227, (1922).

The effect of the temperature of firing siliceous materials is shown in Table CLXII, due to Houldsworth and Cobb.

TABLE CLXII.—*Effect of Firing on Silica.* (*Coefficient of Linear Expansion* $\times 10^{-7}$)

Material.	Temperature Range.	Temperature of Firing.			
		Cone 06.	Cone 9.	Cone 14.	Cone 20.
Meanwood ganister (no bond) .	15–1000	..	107	104	107
,, ,, (lime bond) .	,,	75	68	55	62
Welsh quartzite (lime bond) .	,,	122	128	155	153
Flint (lime bond) . . .	15– 900	136	146	146	168
Pure amorphous silica . .	15–1000	166 [1]	..	224	..
Precipitated silica with 5 per cent. soda	,,	..	92	..	..

According to J. W. Mellor,[2] at high temperatures the coefficient of expansion of silica bricks is greater than at lower temperatures, the average difference being as follows :—

15–940° C. . . .	0·0000051
15–1180° C. . . .	0·0000064

Fused silica has a very low coefficient of expansion at 1100° C.; it is only 0·00000059 or $\frac{1}{7}$ that of ordinary glass, so that it is very insensitive to sudden changes of temperature and can be quenched from red heat in cold water without fracture.

Table CLXIII shows the coefficient of expansion of fused silica when heated to different temperatures.

TABLE CLXIII.—*Coefficient of Expansion of Fused Silica*

Temperature, ° C.	Coefficient of Linear Expansion.	Authority.
—191–16	0·000000256	F. Henning.
16–250	0·000000539	,,
16–1000	0·000000540	,,
200	0·000000518	Randall.
500	0·000000563	,,
900	0·000000538	,,
1100	0·000000583	,,
0–1000	0·000000700	Le Chatelier.

[1] Fired at 1170° C.

[2] *Trans. Eng. Cer. Soc.*, **16**, 268 (1916–17).

Holborn and Henning later found that the expansion of silica glass between 0° and 1000° C. is proportional to the temperature, and approximated to 54×10^{-8}. Common glass has an expansion of $600-900 \times 10^{-8}$.

Fused bauxite has, according to B. Bogitch,[1] a smaller thermal expansion from 0°–1600° C. than clay, silica, chromite, and magnesia.

Alundum, according to Boeck,[2] has a coefficient of expansion of 866×10^{-8} between 100° and 900° C.

Magnesia bricks, up to 1400° C., have a temporary expansion of about 1·9–1·95 per cent.

Recrystallised crystolon between 100° and 900° C. has, according to Boeck, a coefficient of expansion of 474×10^{-8}.

It will be realised that the changes which occur in the volume of ceramic materials when heated cannot be expressed in any simple terms. They are affected by so many factors that they cannot be summarised in any simple "law." The nearest approach to such a summary is that suggested by J. W. Mellor, and described on p. 566, but its use is, unfortunately, limited.

Effects of Sudden Changes in Temperature

The ability of ceramic materials to resist sudden changes in temperature depends upon :

(*a*) Their *permanent and reversible expansion or contraction.*

(*b*) Their *texture*, including the size and shape and grading of the grains (see also Chapter II).

(*c*) Their *porosity* (see also Chapter II).

In a perfectly burned material the resistance would depend wholly upon the reversible expansion, but in practice this is never the case (except possibly with fused silica), because, unless the burning is carried to completion (*i.e.* to the fusion of the whole of the material), the reactions between the various components will not be complete and will proceed further whenever the material is heated to a sufficiently high temperature. Hence, the so-called "permanent" change in volume often has a great influence on the sensitiveness of the ware to sudden changes in temperature.

Fine-grained masses are less resistant to temperature changes than coarse-grained ones, because the interstices between the fine grains are too small to enable the particles to accommodate themselves to the stresses placed upon them by local contractions or expansions, and also because the bond uniting the particles is weaker than the particles themselves. Masses composed of much coarser grains have larger interstices between the grains and are able to rearrange themselves as the temperature rises or falls. The difference in size of grain is of less importance when the particles are tightly interlocked with very little space between them, as they are then unable to move freely when sudden changes of temperature occur and, consequently, shattering of the mass results along the line of least resistance.

[1] *Comptes Rend.*, **173**, 1358–60 (1921). [2] *Loc. cit.*, p. 521.

Whilst the foregoing statement is correct in the majority of cases, it must not be supposed that fine grains and low porosity are always accompanied by great susceptibility to sudden changes of temperature, because some articles having such a structure are very durable in use, even under violent changes in temperature.

Fireclay bricks are not so susceptible to sudden changes of temperature as are silica bricks,[1] but if heated or cooled too rapidly they crack. The most resistant fireclay bricks are those which are most porous. Grog bricks are less likely to crack than fireclay bricks made wholly of clays, and sillimanite bricks—in which most of the clay has been converted into crystalline sillimanite—are still more resistant to sudden changes in temperature. Fireclay bricks of good quality and reasonably porous should not lose more than 12 per cent. by weight when subjected to the spalling test described on p. 523, but bricks having a very close texture may lose up to 65 per cent. by weight.

Large blocks are more susceptible to sudden changes in temperature than are smaller ones, but if properly made they should resist all ordinary conditions of heating and cooling. To secure the necessary resistance they should have a more open texture (p. 38) than is needed for bricks or small blocks, so that the pores may take up any strains which occur.

Saggers made of fireclay must be reasonably constant in volume when in use or they may warp and lose their shape. This will cause them to fit badly on one another and possibly endanger the stability of the " bungs " of saggers placed one above another in the kiln. Saggers should be as porous as is consistent with the necessary strength (p. 78).

Glass-melting pots and **retorts** require to be very resistant to sudden changes in temperature, but it is difficult to secure this property at the same time as a high resistance to corrosion. Moderately porous materials are the most suitable for the purpose where the corrosion is not excessive.

Crucibles must be very resistant to sudden changes of temperature, as when in use they are withdrawn rapidly—from a furnace (which may have a temperature up to 1800° C.) into the open air. This resistance is attained if the crucible has an open, porous texture (p. 39), which may be obtained in the case of fireclay crucibles by introducing a sufficiently large proportion of grog into the mixture of which the crucibles are made. The number of times which a crucible can be re-heated varies according to its contents and the manner in which it is used. The following figures show the average " life " if the crucibles are properly handled :—

TABLE CLXIV.—*Durability of Crucibles when Melting Metals*

Nature of Contents.	Number of Heatings.	Nature of Contents.	Number of Heatings.
Brass . . .	70–100	Iron . . .	70–90
Bronze . .	about 50	Steel . . .	6–10

[1] The manufacturers of Glenboig firebricks claim that these bricks may be dropped whilst red hot into cold water without being cracked. No silica bricks will withstand so severe a test.

The crucibles used for making steel do not last long on account of the very high temperatures (about 1550° C.) reached in melting the metal.

Silica bricks are very susceptible to sudden changes in temperature and soon develop fine cracks, which later increase in size and cause the bricks to become weak or to spall and flake. Most silica bricks are so sensitive to changes in temperature, that if a current of air is drawn through them during the cooling of the kiln they are liable to crack. For this reason, after the firing of the bricks is completed, the kilns are closed and allowed to cool in such a manner that the whole of the heat is lost by radiation through the walls and floor of the kiln. Continuous kilns are seldom used for silica bricks, because they require a current of air to pass through them.

The great liability of silica bricks spalling at temperatures below 500° C. is due to the α–β transition range described on p. 329.

As cristobalite and tridymite are the forms of silica which are stable at high temperatures, whereas quartz is the unstable form, silica bricks which have been burned in such a manner that most of the quartz has been converted into tridymite and cristobalite are more constant in volume than those which have not been sufficiently fired, and the former are much less likely to crack when subjected to sudden changes in temperature.

Silica bricks are not resistant to sudden heating and cooling, and when subjected to the test described on p. 523 they are destroyed in less than ten heatings.

Bauxite bricks are liable to crack when exposed to sudden changes of temperature unless they have been made of very well-burned material. Bricks made of fused alumina are much more resistant to sudden changes in temperature than bricks made of calcined bauxite, the best results being obtained when the alumina is in large crystals.

Magnesia bricks are particularly subject to spalling, this being due, according to J. W. Mellor,[1] to :

(*a*) The shrinkage caused by the conversion of α- into β-magnesia (*i.e.* of lightly calcined magnesia into periclase, p. 356), and

(*b*) The shrinkage caused by the closing of the pores.

Bricks of low porosity are less likely to spall, but all bricks made of this material suffer to a greater or less extent from this very serious drawback. By enclosing the material in iron cases—as in the " Metalkase " bricks—the drawbacks due to excessive cracking are largely prevented.

Zirconia bricks and crucibles are very resistant to temperature changes and, for this reason, their use may increase in the near future.

Chromite bricks, according to Hartmann and Hongen, are very susceptible to sudden changes of temperature, and are wholly disintegrated by the spalling test described on p. 523.

Carbon bricks are quite insensitive to sudden changes of temperature as their coefficient of expansion is very low.

Carborundum bricks are also very insensitive, especially those made from

[1] *Trans. Eng. Cer. Soc.*, **16**, 85 (1916–17).

carbofrax, which Hartmann and Hongen [1] found to lose only 0·3–8 per cent. of their weight when subjected to the very stringent test described on p. 523.

Table CLXV shows the results obtained by Hartmann and Hongen for the resistance of various refractory materials to spalling, the test-pieces being heated to 1350° C., and then cooled rapidly by means of a blast of air.

TABLE CLXV.—*Effect of Rapid Cooling on Spalling*

Kind of Brick.	No. of Coolings.	Loss by Spalling, per cent.
Bonded carborundum (Carbofrax A) .	10	0·3
,, ,, (,, B) .	10	6
,, ,, (,, C) .	10	8
Recrystallised carborundum (Refrax) .	10	12
Bauxite	10	43
Zirconia (natural)	10	53
Fireclay, Grade A	10	9
,, ,, B	10	65
,, ,, C	10	90
Chromite bricks	7	100
Silica bricks	4	100
Magnesia bricks	3	100

EFFECT OF HEAT ON THERMAL CONDUCTIVITY

The effect of heat on the thermal conductivity (p. 514) of ceramic materials and the various other equivalents of this property, such as resistivity, diffusivity, etc., are very important when the materials are required either to act as heat insulators and prevent the escape of heat from furnaces, etc., or as conductors which allow heat to pass through them from a source of heat situated on one side or externally to the article or materials to be heated on the other side or internally. The use of heat-insulators is typified in the case of furnaces and kilns of all kinds, as the heat is required to be applied to their contents and not allowed to escape unnecessarily to the open air. The use of ceramic materials as thermal conductors is typified by their employment as retorts, muffles, saggers, or crucibles, the contents of which are heated, all flames, etc., being arrested by the ceramic material.

The rate at which heat passes through ceramic materials may be expressed in different ways, according to the purpose for which they are used, see p. 515.

Conclusions and deductions based on the thermal conductivity or resistivity of a ceramic material must be used with great caution, as various other factors may

[1] *Brick and Clay Record*, **56**, 934 (1920).

require to be taken into consideration. For instance, the thermal conductivity of firebricks used under oxidising conditions is quite different from that when the same bricks are employed under reducing conditions ; in the latter case they may quickly become coated with a layer of carbon (" retort graphite ") which entirely alters their behaviour with respect to the transmission of heat.

As explained on p. 514, the rate at which heat passes through a ceramic material either by radiation or conduction is directly proportional to its temperature, though this statement must usually be modified on account of the influence of other factors.

The effect of heat on the thermal conductivity of a material may be considered with respect to :

(i) The heat applied in course of manufacture (*i.e.* in the burning of ceramic ware).

(ii) The temperature of the material when in use.

The heat applied during the course of manufacture is very important, as the thermal conductivity usually increases with the temperature of firing. This is often due to the pore spaces being reduced in size and number by being filled with the fused material produced during the burning of the ware at a high temperature. Prolonged burning has a similar effect. The best heat-insulating qualities are obtained, according to A. L. Queneau, by burning the materials at the lowest possible temperature consistent with their satisfactoriness in use.

Table CLXVI [1] shows the effect of the burning temperature on the thermal conductivity of various refractory materials.

TABLE CLXVI.—*Effect of Burning Temperature on Thermal Conductivity*

	Burning Temperature, ° C.	Gm.-cals.	Kg.-cals.	Porosity, per cent.
Fireclay bricks . .	1050	0·0035	1·25	29·4
,, . .	1200	0·0030	1·07	..
,, . .	1300	0·0050	1·81	24·1
,, . .	1300	0·0042	1·50	30·2
Fireclay retorts . .	1300	0·0038	1·37	27·3
Bauxite bricks . .	1050	0·0031	1·11	41·5
,, . .	1300	0·0033	1·19	38·4
Silica bricks . . .	1050	0·0020	0·71	42·5
,, . . .	1300	0·0031	1·12	42·9
Magnesia bricks . .	1050	0·0058	2·08	35·1
,, . .	1300	0·0065	2·35	41·0
Chromite . . .	..	0·0066	2·37	..
Graphite . . .	..	0·0250	9·00	..
Kieselguhr . . .	..	0·0018	0·64	58·0
Hard porcelain . .	1400	0·0043	1·55	..

[1] Wologdine.

The thermal conductivity of carborundum increases very rapidly when it is burned at higher temperatures, thus :—

TABLE CLXVII.—*Thermal Conductivity of Carborundum*

Burning Temperature, ° C.	Thermal Conductivity, gm.-cals.
1050	0·0033
1300	0·0145

This represents an increase of nearly 400 per cent. ; the thermal conductivity of magnesia under the same conditions and within the same range of temperature increases only 5 per cent.

The temperature of a ceramic material when in use has also a very important influence on the thermal conductivity. In most cases, the conductivity increases at high temperatures, the extent of the increase depending on the nature of the material. Thus, the thermal conductivity of fireclay and grog bricks increases considerably when they are heated to 1200° C., whereas that of chromite bricks is hardly affected, and that of magnesia bricks decreases slightly at high temperatures.

Table CLXVIII, due to R. H. Horning, shows the relative thermal conductivity of various refractory materials.

TABLE CLXVIII.—*Thermal Conductivity of Refractory Materials at Various Temperatures*

Material.	Wt. in lbs. per cu. ft.	Temperature Difference in ° C.													
		200.	300.	400.	500.	600.	700.	800.	900.	1000.	1100.	1200.	1300.	1400.	1500.
Magnesia bricks .	164·0	268	273	276	280	284	288	292	296	300	302	305	307	309	310
Silica bricks . .	97·0	123	127	132	136	139	142	145	148	151	153	154	156	158	159
No. 1 firebrick .	131·0	52	57	62	66	70	74	77	81	83	85	86·5	87	87·5	87·5
Repressed burned kieselguhr brick .	23·2	24	25	26	26	26·5	27	27·5	27·7	28	28·1	28·2	28·5	28·5	28·5
Natural kieselguhr brick (perpend. to grain) . .	33·0	19·9	20	20·5	21	21·5	21·9	22·3	22·7	23·1	23·5	23·9	24·3	24·7	25·2
Nonpareil insulating brick . .	24·0	13	14·4	15·6	16·8	17·8	18·8	19·6	20·1	20·6	21	21·4	21·7	22·0	22·2

The following information relates specifically to the particular ceramic articles mentioned :—

Clay wares have a thermal conductivity depending on their texture, those which are vitrified being usually better conductors than those which are more porous. The thermal conductivity of fireclay bricks is almost always less than 0·0050 gram-cals., and is usually about half this figure; the thermal conductivity of building bricks is similar. Table CLXIX, due to L. R. Ingersoll,[1] shows the average diffusivity of fireclay bricks in comparison with other materials, including some metals :—

TABLE CLXIX.—*Thermal Conductivity of Various Materials*

Material.	Diffusivity.	Material.	Diffusivity.
Air . . .	0·1800	Gold . . .	1·1800
Building brick .	0·0050	Iron . . .	0·1700
Cast steel . .	0·1200	Silica brick .	0·0030
Copper . .	1·1300	Silver. . .	1·7400
Firebrick . .	0·0067		

The figure given above for a firebrick differs considerably from those obtained by A. T. Green[2] and shown in Table CLXX, but it agrees fairly closely with the figures obtained by Dougill, Hodsman, and Cobb and shown in Table CLXXI.

The thermal conductivity rises on heating the material, especially if the temperature rises above 900° C. Thus, Table CLXX shows the figures obtained by A. T. Green[2] for the increase in thermal conductivity and diffusivity of fireclay bricks at the temperatures mentioned :—

TABLE CLXX.—*Effect of Temperature on Conductivity and Diffusivity of Fireclay Bricks*

Temperature, ° C.	Thermal Conductivity, gm.-cals. per sec.	Diffusivity.
500	0·0010	0·0020
600	0·0011	0·0021
700	0·0013	0·0023
800	0·0015	0·0025
900	0·0016	0·0026
1000	0·0018	0·0027
1100	0·0025	0·0034

[1] Communication to Harvard.

[2] *Loc. cit.*, p. 515.

Dougill, Hodsman, and Cobb obtained much higher figures for both thermal conductivity and diffusivity, as shown in Table CLXXI.

TABLE CLXXI.—*Effect of Temperature on Conductivity, etc.*

Material.	Temperature, ° C.	Heat Conductivity, gm.-cals. per sec.	Specific Gravity.	Specific Heat.	Heat Diffusivity.
Firebrick . .	500	0·0028	1·95	0·23	0·0062
,, . .	1000	0·0040	..	0·26	0·0079
Silica brick .	500	0·0024	1·74	0·26	0·0053
,, .	1000	0·0046	..	0·27	0·0098
Magnesia brick .	500	0·0141	2·40	0·26	0·0226
,, .	1000	0·0085	..	0·28	0·0126

They suggest the following formula for calculating the thermal conductivity of fireclay bricks up to 1000° C. :—

$$Kt = 0{\cdot}00155 + 0{\cdot}25 \times 10^{-5}t,$$

where Kt is the thermal conductivity of the material in grams-cals. per sec. at $t°$ C.

Table CLXXII gives the results obtained by Heyn, Bauer, and Wetzel [1] for the thermal conductivity of grog bricks in comparison with other refractory materials, at different temperatures.

TABLE CLXXII.—*Thermal Conductivity of Grog and Other Bricks*

Material.	Specific Gravity.	Thermal Conductivity in gm.-cals. per cm. per sec.					
		200° C.	400° C.	600° C.	800° C.	1000° C.	1200° C.
Grog brick . .	1·88	0·0014	0·0018	0·0022	0·0024	0·0026	0·0027
,, . .	1·30	0·0011	0·0014	0·0016	0·0019	0·0021	..
,, . .	1·77	0·0009	0·0011	0·0012	0·0013	..	..
,, . .	1·90	0·0021	0·0024	0·0027	0·0027	0·0027	0·0027
Dinas brick . .	2·04	0·0013	0·0016	0·0017	0·0017	0·0018	0·0021
Magnesia brick . .	2·35	0·0011	0·0015	0·0012	0·0013	0·0014	0·0014
Carbon brick . .	1·27	0·0012	..	..	..	..	..

Retorts, muffles, and **saggers** require to have as high a thermal conductivity

[1] *Berlin Bur. Stand.*, 1914 ; *Sprech.*, **52**, 499–501 (1919).

as possible, so as not to waste fuel in heating them rather than their contents. Complete satisfaction is very difficult to obtain as the highest thermal conductivity is associated with materials which are dense in texture, whereas resistance to the changes in temperature to which such articles are exposed necessitates the use of a porous mass. The influence of temperature on the thermal conductivity of gas retorts is shown in Table CLXXIII, due to Wologdine, whilst in Table CLXXIV corresponding figures obtained by A. T. Green are shown.

TABLE CLXXIII.—*Thermal Conductivity of Retorts*

Temperature of Upper Surface, ° C.	Temperature of Lower Surface, ° C.	Thermal Conductivity, gm.-cals. per cm. per sec.
140	1120	0·0040
175	1110	0·0040
160	1050	0·0039
150	1010	0·0040
140	990	0·0038
151	870	0·0037
105	685	0·0035

TABLE CLXXIV.—*Thermal Conductivity of Retorts*

Temperature, ° C.	Thermal Conductivity, gm.-cals. per sec.	Thermal Diffusivity.
500	0·0008	0·0017
600	0·0009	0·0018
700	0·0010	0·0020
800	0·0012	0·0022
900	0·0013	0·0022
1000	0·0014	0·0023
1100	0·0017	0·0026

The thermal conductivity of **refractory porcelain** is about 0·002–0·004, or rather higher than that of glass.

Lees and Chorlton found the thermal conductivity of a sample of porcelain tested to be 0·00248 between 92° C. and 98° C.

Silica bricks are usually considered to be better conductors of heat than fireclay bricks, though opinion is divided on the matter. Thus, some Dinas silica bricks

have a thermal conductivity of about 0·0013 gram-cals. at 200° C., to about 0·0021 gram-cals. at 1200° C. (see Table CLXXII), but Gœrens and Giles found that the thermal conductivity of other silica bricks is greater than that of fireclay bricks, except those made from Lias clay, as shown in Table CLXXV, whilst G. H. Brown [1] gives the relative conductivities of silica, quartzite (ganister), and fireclay bricks as 1017, 986, and 933 respectively. This represents the conductivity of silica bricks as 9 per cent. greater and quartzite bricks as 52 per cent. greater than that of fireclay bricks. Other investigators, however (including Wologdine, Dougill, Hodsman and Cobb, Heyn, Bauer and Wetzel, and A. T. Green), consider that silica bricks sometimes have a lower conductivity than fireclay bricks.

TABLE CLXXV.—*Thermal Conductivity of Silica and other Bricks*

Material.	Average Coefficient of Thermal Conductivity, cal. per metre per hour per 1° C.	Material.	Average Coefficient of Thermal Conductivity, cal. per metre per hour per 1° C.
Semi-grog . .	0·90	Lias clay . .	1·76
Grog . .	0·91	Silica . .	1·11
Shale . .	0·99		

Commercially, there is probably very little to choose between the thermal conductivities of fireclay and silica bricks, as the figures obtained with different samples vary as a result of differences in texture, burning temperature, etc. Hence, the greater speed with which heat appears to pass into silica retorts is probably due to their greater diffusivity rather than to their thermal conductivity, as is commonly supposed.

The influence of the temperature of burning on the thermal conductivity of silica bricks is shown in Table CLXVI. Silica bricks with the lowest thermal conductivity are those in which the quartz is not converted into tridymite or cristobalite. According to A. L. Queneau, silica bricks burned at about 1050° C. are as resistant to the passage of heat as kieselguhr bricks, and have only one-half the conductivity of fireclay bricks. This may not be entirely correct, as the variations in thermal conductivity in different bricks are so great.

Silica bricks increase considerably in conductivity when heated, as shown by the results obtained by A. T. Green in Table CLXXVI.

Other results are given in Tables CLXIX and CLXXI, including those of Dougill, Hodsman, and Cobb, who have obtained much higher results for both diffusivity and thermal conductivity.

Light-weight silica bricks have a lower thermal conductivity than ordinary ones.

[1] *Trans. Amer. Cer. Soc.*, **16**, 382 (1914).

TABLE CLXXVI.—*Effect of Heat on Conductivity and Diffusivity of Silica Bricks*

Temperature, ° C.	Conductivity, gm.-cals. per sec.		Diffusivity.	
	A.	B.	A.	B.
500	0·0007	..	0·0017	..
600	0·0008	0·0009	0·0018	0·0024
700	0·0009	0·0011	0·0019	0·0026
800	0·0010	0·0012	0·0019	0·0028
900	0·0011	0·0014	0·0020	0·0030
1000	0·0013	0·0017	0·0022	0·0033
1100	0·0016	0·0020	0·0025	0·0037

Those made by J. H. Sankey & Son, Ltd., are claimed to have a heat conductivity of 0·0005 C.G.S. units.

Kieselguhr bricks have a thermal conductivity of about 0·0018 gram-cals., which is about half that of fireclay bricks.

Silica glass or **fused silica** has (when cold) a thermal conductivity of about 0·002–0·003 C.G.S. units.

Magnesia bricks have about twice the thermal conductivity of fireclay bricks, and also a very high heat-diffusivity, but their great sensitiveness to sudden changes of temperature is a serious disadvantage.

The temperature at which magnesia bricks have been burned has only a slight influence on the thermal conductivity as shown in Table CLXVI. The results obtained by A. T. Green are shown in Table CLXXVII.

TABLE CLXXVII.—*Conductivity and Diffusivity of Magnesia Bricks*

Temperature, ° C.	Thermal Conductivity, gm.-cals. per sec.	Diffusivity, C.G.S. Units.
500	0·0017	0·0023
600	0·0017	0·0021
700	0·0017	0·0020
800	0·0017	0·0019
900	0·0016	0·0017
1000	0·0016	0·0017
1100	0·0016	0·0016

It will be seen that the thermal conductivity of magnesia bricks is almost constant, or decreases very slightly at high temperatures.

Dougill, Hodsman, and Cobb, in Table CLXXI, show a similar decrease, but their results are much higher. They suggest the following formula for calculating the thermal conductivity of magnesia bricks up to 1000° C. :—

$$K_t = 0{\cdot}0285 - 0{\cdot}379 \times 10^{-4}t - 0{\cdot}179 \times 10^{-7}t^2,$$

where K_t is the thermal conductivity in gram-cals. per sec. at $t°$ C.

Heyn, Bauer, and Wetzel show a slight increase in conductivity at high temperatures in Table CLXXII.

Chromite bricks, according to A. L. Queneau, have practically the same thermal conductivity at all temperatures, namely, 0·0057 C.G.S. units.

Carborundum bricks have a high thermal conductivity ; even when mixed with as much as 20 per cent. of clay they conduct three times as much heat as magnesia bricks, seven times as much as fireclay bricks, and twelve times as much as silica bricks in a given time.

Graphite bricks, according to Heyn, Bauer, and Wetzel (Table CLXXII), have about five times the thermal conductivity of fireclay bricks, viz. about 0·0012 C.G.S. units.

TABLE CLXXVIII.—*Thermal Conductivity of Powders*

Material.	Thermal Conductivity in gm.-cal. sec. per cm.^{3} per 1° C.
White Calais sand	0·00060
Fine carborundum	0·00050
Coarse ,,	0·00051
Enamel quartz	0·00036
Fused quartz	0·00039
Fireclay brick	0·00028
Retort graphite	0·00040
Lime	0·00029
Fused magnesia	0·00047
Mabor magnesia brick	0·00050
Calcined Greek magnesia	0·00045
Calcined Veitsch magnesia	0·00034
Pattinson's high calcined magnesia	0·00016
Kieselguhr	0·00013

When bricks or blocks are cemented together to form a wall, as in a furnace, the

thermal conductivity may be much altered, and Dougill, Hodsman, and Cobb have pointed out that the thermal conductivity of the joints of brickwork is only one-tenth that of the bricks themselves, so that segmental retorts would appear to require more heat than those in one piece, if both kinds of retorts are made of the same material.

Table CLXXVIII, due to Harvard, shows the thermal conductivity of various raw ceramic materials in C.G.S. units between 20° C. and 100° C., the materials in each case being in the form of a powder which passed entirely through a sieve with 600-meshes per square cm. (approximately 60 meshes per linear inch).

Table CLXXIX, also due to Harvard, shows the thermal conductivity of various commercial refractory, and other bricks and blocks, between 1000° and 1200° C.

TABLE CLXXIX.—*Thermal Conductivity of Bricks*

Material.	Gm.-cal. sec. per cm.^{3} per 1° C.	Kg.-cal. hour per m.^{3} per 1° C.	Relative Conductivity.
Graphite brick	0·0250	9·00	100·0
Carborundum brick	0·0231	8·32	92·4
Magnesia brick	0·0071	2·54	28·4
Chromite brick	0·0057	2·05	22·8
Fireclay brick	0·0042	1·50	16·7
Checker brick	0·0039	1·42	15·8
Gas retort brick	0·0038	1·36	15·2
Building brick	0·0035	1·26	14·0
Glass pot	0·0033	1·19	13·2
Bauxite brick	0·0027	0·96	12·4
Terra-cotta	0·0023	0·84	9·3
Silica	0·0020	0·71	7·8
Kieselguhr	0·0018	0·64	7·1

There is an unfortunate lack of information on the thermal conductivity of refractory materials at the temperatures at which they are chiefly employed, viz. above 1000° C. This is the more regrettable, as a large amount of work has been done at lower temperatures, which is, apparently, of little practical importance.

As the thermal conductivity varies greatly at different temperatures, it is seldom possible to obtain an accurate result by extrapolating from data relating to lower temperatures.

It is often convenient to express thermal conductivity as its converse or reciprocal, *i.e.* as *thermal resistivity* (p. 515) as in Table CLXXX compiled by Hering, which shows the thermal resistivity of various materials.

TABLE CLXXX.—*Thermal Resistivity*

Material.	Thermal Ohms.		Authority.
	in. cube.	cm. cube.	
Silver, 0–100° C.	0·094	0·24	Landolt and Boernstein.
Platinum, 18–100° C.	0·55	1·4	„ „
Acheson graphite, 100°–390° C. (mean)	0·28	0·71	C. Hering.
„ „ 100°–914° C. „	0·32	0·82	„
Electrode carbon, 100°–360° C. „	0·05	2·7	„
„ „ 100°–942° C. „	0·72	1·9	„
Plumbago brick, 1000° C. approx.	3·8	9·6	Wologdine and Queneau.
Carborundum brick „	4·1	10·3	„ „
Quartz	5·9	15·0	Landolt and Boernstein.
Retort carbon, 0° C.	9·1	23·0	„ „
Magnesia brick (about 1000° C.)	13·0	34·0	Wologdine and Queneau.
Chromite brick „	16·0	42·0	„ „
Firebrick „	22·0	57·0	„ „
Chequer brick „	24·0	61·0	„ „
Gas retort brick „	25·0	63·0	„ „
Building brick „	29·0	72·0	„ „
Glass pot „	35·0	89·0	„ „
Porcelain, 95° C.	38·0	96·0	Landolt and Boernstein.
Firestone	39·0	99·0	„ „
Terra-cotta (about 1000° C.)	41·0	104·0	Wologdine and Queneau.
Silica brick „	47·0	120·0	„ „
Kieselguhr brick „	52·0	133·0	„ „
Plumbago, 200–155° C., 26·1 per cent. solid matter	96·0	240·0	Ordway.
Fine sand „ 51·4 „ „	109·0	276·0	„
Coarse sand „ 52·9 „ „	110·0	280·0	„
Pumice „ 34·2 „ „	219·0	558·0	„
Asbestos „ 8·1 „ „	139·0	353·0	„
Kieselguhr „ 11·2 „ „	435·0	1110·0	„
„ „ 6·0 „ „	472·0	1200·0	„
Magnesia, calcined „ 28·5 „ „	160·0	407·0	„
„ „ „ 4·9 „ „	544·0	1380·0	„
„ „ „ 2·3 „ „	544·0	1410·0	„

EFFECT OF HEAT ON THE SPECIFIC HEAT OF CERAMIC MATERIALS

The heat capacity of ceramic materials is often very important and especially when they form part of the walls of furnaces, etc., as all the heat absorbed by such material is, in a sense, wasted and ought to be used in heating the contents of the furnace.

The various terms "heat capacity," "atomic," "molecular" and "specific heats" have been defined on pp. 510–514, and the methods of determining them have also been described on p. 512.

The specific heat of most materials increases with the temperature, so that the fuel consumption when heating ceramic materials at high temperatures is much greater than that at low temperatures, the same weight of material being used in each case. Thus, in fireclay bricks, according to Bradshaw and Emery,[1] the relation between the fuel consumption at 1200°–1400° C. and that at 100°–300° C. is nearly 3 : 2.

Clays.—J. M. Knote [2] found the specific heat of raw clay to be about 0·237, that of clay heated to 650° C. 0·204, and that burned at 1050° C. to be 0·200 C.G.S. units.

It will be seen that the dehydration of clay causes a decrease in the specific heat. The specific heat at 1050° C. is practically the same as that at 650° C., the difference being due probably to the water not completely removed during the decomposition at 650° C.

The specific heat of *kaolin* at different temperatures is shown in Table CLXXXI according to various authorities.

TABLE CLXXXI.—*Changes in Specific Heat of Kaolin*

Temperature, ° C.	Specific Heat.	Authority.
..	0·235	J. M. Knote.
22–98	0·2242	L. Boernstein.
440–1000	0·235	Bleininger and Moore.
650	0·204	J. M. Knote.
1050	0·200	,,

The specific heat of fireclay bricks at different temperatures may, according to S. T. Wilson and A. D. Holdcroft,[3] be calculated from the formula :

$$\text{Sp. ht.} = 0{\cdot}193 + 0{\cdot}00006t,$$

where t is the temperature in ° C. Table CLXXXII shows some experimental results obtained by the same investigators.

TABLE CLXXXII.—*Variations of Specific Heat with Temperature*

Temperature, ° C.	Average Specific Heat.	Temperature, ° C.	Average Specific Heat.
700	0·233	1100	0·255
800	0·241	1200	0·261
900	0·246	1300	0·264
1000	0·263		

[1] *Trans. Eng. Cer. Soc.*, **19**, 88 (1919–20). [2] *Trans. Amer. Cer. Soc.*, **14**, 394 (1912).
[3] *Trans. Eng. Cer. Soc.*, **12**, 279 (1913).

Bradshaw and Emery[1] have found that the specific heat of fireclay bricks at different temperatures is correctly shown by the formula :

$$0{\cdot}193+0{\cdot}000075t,$$

where t is the temperature in ° C. This is about 25 per cent. higher than Wilson and Holdcroft's figure (p. 595).

Table CLXXXIII, due to Bradshaw and Emery,[1] shows the specific heats of various materials between 25° and 1400° C.

TABLE CLXXXIII.—*Specific Heats of Various Bricks*

Temperature, ° C.	Coarse Silica Brick.	Fine Silica Brick.	Firebrick.	Zirconia Pure.	Stourbridge Firebrick (Wilson and Holdcroft).
600	0·226	0·228	0·228	0·137	0·227
1000	0·263	0·262	0·265	0·157	0·263
1200	0·282	0·283	0·284	0·167	0·262
1400	0·293	0·295	0·297	0·175	..

Table CLXXXIV, due to Heyn, Bauer, and Wetzel,[2] shows the specific heat of grog bricks in comparison with various other materials at different temperatures.

TABLE CLXXXIV.—*Specific Heat of Refractory Bricks*

Material.	Specific Gravity.	Specific Heat at					
		200° C.	400° C.	600° C.	800° C.	1000° C.	1200° C.
Grog brick .	1·88	0·225	0·250	0·272	0·287	0·298	0·305
,, .	1·30	0·216	0·254	0·273	0·287	0·295	0·300
,, .	1·77	0·217	0·243	0·263	0·281	0·295	0·304
,, .	1·90	0·223	0·262	0·284	0·291	0·292	0·293
Dinas brick .	2·04	0·237	0·270	0·282	0·285	0·288	0·291
Magnesite brick	2·35	0·258	0·275	0·291	0·307	0·324	0·340
Carbon brick .	1·27	0·312	0·358	0·377	0·395	0·412	..

The specific heat of unglazed Berlin porcelain is, according to W. Steger, 0·202, C.G.S. units, between 20° and 200° C. and 0·221 between 200° and 400° C.

[1] *Loc. cit.*, p. 595.

[2] *Loc. cit.* p. 588.

Siliceous Materials.—Table CLXXXV, due to W. P. White, shows the specific heat of various forms of silica.

TABLE CLXXXV.—*Specific Heat of Various Forms of Silica*

Temperature, ° C.	Quartz Glass.	α-Quartz.	β-Quartz.	Cristobalite.
100	0·202	0·204	..	..
250	0·236	0·244	..	..
500	0·266	0·294	..	..
550	..	0·313	..	..
750	0·280	..	0·277	0·278
1000	0·290	..	0·288	0·285
1100	..	..	..	0·287

Ulrich [1] gives the specific heat of quartz sand between 20° and 98° C. as 0·191.

The specific heats of silica and fireclay bricks are very similar, generally about 0·26. The specific heats of various silicates is shown in Table CLXXXVI, due to W. P. White.[2]

TABLE CLXXXVI.—*Specific Heat of Various Substances*

Temperature.	Pseudo-Wollastonite.	Wollastonite.	Orthoclase.	Diopside.	Quartz.	Orthoclase Glass.	Soft Glass.
100	..	0·1833	..	0·1919	0·1840	..	0·1977
500	0·2159	0·2180	0·2248	0·2310	0·2372	0·2291	0·2400
700	..	0·2286	..	0·2420	0·2547	..	0·2646
800	..	..	0·2401	..	..	0·2465	..
900	..	0·2354	..	0·2499	0·2597	..	0·2791
1100	0·2380	0·2423	0·2505	0·2562	0·2643	0·2588	0·2907
1300	0·2422	..	..	0·2613	..	..	0·2945
1500	..	..	..	..	..	..	0·2999

The increase in the specific heat of a material at high temperature is very noticeable.

Barus gives the specific heats of solid and molten diabase as shown in Table CLXXXVII.

[1] *Wollny's Forsch.*, **17**, 1 (1894).

[2] *Amer. J. Sci.*, **28**, 334.

TABLE CLXXXVII.—*Effect of Fusion on Specific Heat*

Temperature.	State.	Specific Heat.
800°–1100° C. . .	solid	0·304
1200°–1400° C. . .	liquid	0·350

The specific heats of various silicates, etc., present in bricks naturally modify the total specific heat, but they are usually present in such small quantities that they do not cause any appreciable difference in the specific heat of the material.

The molecular heats of quartz and various silicates are shown in Table CLXXXVIII.

TABLE CLXXXVIII.—*Molecular Heat of Silica and Silicates (between 15° and 100° C.)*

Substance.	Molecular Heat.	Observer.
Quartz	11·1	White.
$CaSiO_3$	21·4	,,
$PbSiO_3$	22·1	Schulz.
$Na_2OAl_2O_36SiO_2$ . .	104·9	Joly.
$K_2OAl_2O_34SiO_2$ . .	84·3	,,
$Li_2OAl_2O_34SiO_2$ . .	80·8	Schulz.

Alumina has a specific heat (according to Russell [1]) of 0·200 between 3 and 48° C. and (according to H. v. Wartenburg and G. Wetzel [2]) a molecular heat of 10·8 at 230° absolute (−43° C.) and 29·0 at 1308° absolute (1035° C.).

Lime has (according to Laschtschenko [3]) a specific heat of 0·113 between 0° and 150° C. and a molecular heat (according to H. v. Wartenburg and G. Wetzel [2]) of 11·6 at 559° absolute (386° C.) and 13·0 at 1369° absolute (1096° C.).

Magnesia has a specific heat of 0·258 to 0·340 and a molecular heat, according to H. v. Wartenburg and G. Wetzel,[2] of 10·2 at 415° absolute (342° C.) and 14·5 at 1683° absolute (1410° C.).

Zirconia has a remarkably low specific heat; it is, according to Nelson and Petterson [4] only 0·108 between 0 and 100° C.

Holdcroft and Mellor give the following figures for the specific heat of zirconia at different temperatures :—

[1] *Phys. Zeit.*, **13**, 59 (1912).
[2] *Zeits. Electrochem.*, **25**, 209–212 (1919).
[3] *J. Russ. Phys.-chem. Soc.*, **42**, 1604 (1910).
[4] *Ber.*, **13**, 1459 (1880).

TABLE CLXXXIX.—*Specific Heat of Zirconia*

Temperature, ° C.	Specific Heat.	Temperature, ° C.	Specific Heat.
600	0·137	1200	0·164
1000	0·157	1400	0·175

Carbon bricks have a specific heat of about 0·312 at 200° C. and 0·412 at 1000° C.

HEATS OF REACTION IN CERAMIC PROCESSES

The various reactions which take place as a result of chemical affinity cause different heat effects, as described on p. 528. These reactions are often of great importance in the ceramic industries. The principal ones as far as they have been investigated are described in the following pages.

R. C. Ray [1] found that the **heat of solution** of coarsely powdered (20–40-mesh) quartz in a 34·6 per cent. solution of hydrofluoric acid was 30,300 cals. per molecule, whilst that of silica glass in similar sized pieces was 37,300. When more finely ground material (passing a 200-mesh) was used, the results were 32·46, and 36·95 respectively. This suggests that the material is made partly amorphous by grinding it. The higher figures are probably the more correct.

The **heat of formation** of various silicates is shown in Table CXC.

TABLE CXC.—*Heat of Formation of Silicates, etc.*

Silicate.	Heat of Formation, Calories.	Silicate.	Heat of Formation, Calories.
$FeOSiO_2$ . .	10,600	$Al_2O_32SiO_2$ . .	14,900
$2FeOSiO_2$ . .	22,236	$3CaOAl_2O_32SiO_2$.	33,500
$CaOSiO_2$ . .	17,850	Na_2OSiO_2 . .	45,200
$2CaOSiO_2$ . .	28,300	$CaOAl_2O_3$ . .	450
$3CaOSiO_2$ . .	28,250	$3CaOAl_2O_3$ . .	2,950

The **heat of dissociation** is the same as that of formation, but in the reverse direction. Thus, the dehydration of kaolin involves the absorption of 28,900 calories per gram of kaolin.

The small heat effect in the production of mixed crystals is explained by the fact

[1] *Proc. Roy. Soc. London*, **101A**, 509–16 (1922).

that an ion or molecule in one crystal is merely replaced by another with which it is isoteric.

The **heat of transition** of silicates has not, as yet, been fully investigated.

The **latent heat of fusion** of silica calculated according to Richard's and Vogt's formulæ respectively is about 65 calories per gram.

E. W. Washburn [1] calculates the latent heat of fusion of cristobalite from the formula :

$$L = \frac{RT^2x}{\triangle t},$$

where L is the molal heat of fusion, R is the gas constant, T the absolute melting-point of the substance, $\triangle t$ the lowering of the freezing-point in some solution, such as the eutectic between cristobalite and sillimanite (=100° C.) and x the mole-fraction of the solution (alumina or sillimanite) which with sillimanite is 0·0882. From these figures Washburn estimated that the latent heat of cristobalite is 6800 calories per mole, or 110 calories per gram.

E. W. Washburn [2] suggested the use of the following formulæ, in accordance with the freezing-point solubility law, for determining the latent heats of fusion of refractory materials which form eutectics with each other. This law expresses the relation between the composition of a solution and the temperature at which it will be in equilibrium with pure crystals of either of its constituents.

$$\mathrm{Log}_{10}x_a = \frac{0{\cdot}219L_a(T_a - T)}{T_aT}$$

$$\mathrm{Log}_{10}x_b = \frac{0{\cdot}219L_b(T_b - T)}{T_b}$$

where x_a and x_b represent respectively the molecular fractions of the substances A and B in the solution, L_a and L_b represent respectively the latent heats of fusion of one gram-molecular weight (or mole) of the substances A and B, whilst T_a and T_b represent respectively the melting-points of the two pure materials on the absolute scale, and T is the eutectic temperature also on the absolute scale. This method may, however, be inaccurate on account of the possible presence of some unknown factor at high temperatures which brings error into the results. He gives the following figures for the latent heat of fusion of lime and magnesia :—

TABLE CXCI.—*Latent Heat of Fusion*

Substance.	Fusing-point (Kanolt), ° C.	Latent Heat of Fusion per gm.	Latent Heat of Fusion per mol.
Lime	2570±3	490±20 per cent.	30,000
Magnesia . . .	2800±3	700±15 per cent.	30,000

[1] *J. Amer. Cer. Soc.*, 2, 1006 (1919).

[2] *Trans. Amer. Cer. Soc.*, 19, 195 (1917).

The latent heat of fusion of some complex materials is very high, possibly on account of their decomposition at the fusion-point; in that case, the heats of decomposition would be included in the latent heat of fusion.

The latent heat of fusion of silicates is greatest in those which have the highest absolute heat of fusion; it averages about 100 cals. per gram.

Table CXCII shows the heats of fusion of various complex materials.

TABLE CXCII.—*Heats of Fusion of Complex Materials (calculated from the Heating and Cooling Curves)*

Substance.	Melting-point.	Latent Heat of Fusion.		Observer.
	° C.	Per gm.	Per mol.	
Anorthite . .	1200	100	28,000	Vogt.[1]
Diopside . .	1225	100	22,000	Vogt and White.[2]
Enstatite . .	1375	125	25,000	Vogt.
Olivine . . .	1400	130	18,000	,,
Akermanite . .	..	90	..	..
Calcium borate .	..	49	..	..
Leucite . .	..	26	..	..

EFFECTS OF HEAT ON APPARENT REFRACTORINESS

The refractoriness or resistance to heat of a material is defined on p. 525. The apparent resistance to heat is affected by heat in two ways:

(*a*) By the duration and maximum temperature of the burning in course of manufacture; and

(*b*) by the direct effect of heat on the material when in use.

The effect of heat on the refractoriness is largely confined during manufacture to the greater facility with which chemical reactions proceed at high temperatures (Chapter XI), and, consequently, produce compounds of lower refractoriness than that of the substances (taken separately) from which they are formed. The effect of heat on the refractoriness of ceramic materials when in use is the same as that just mentioned, but is largely dependent on the temperature at which the materials are used.

The *true* refractoriness of a material, as defined on p. 525, is constant for any given material, but when two or more substances are brought into contact the refractoriness of the mixture will depend on:

1. The nature of the materials, including the proportion of fluxes (Chapter IX).
2. The size of the grains (p. 30).

[1] *Silikatschmelzlœsungen*, 1904, 65–68, Part 2.

[2] *Z. Anorg. Chem.*, **69**, 348 (1911).

3. The shape of the grains (p. 27).
4. The grading of the material (p. 31).
5. The porosity of the material (p. 74).
6. The permeability of the material (p. 86).
7. The nature of the atmosphere in which the material is heated (p. 525).

Owing to the low thermal conductivity of most ceramic materials, other factors also influence the refractoriness in actual use, though, in determining this property, they are eliminated by using test-pieces of definite size and shape and by raising their temperature at a constant rate (p. 526). The most important of these additional factors are :

8. The previous treatment of the material, which determines the time required for the reactions between the different substances present to proceed sufficiently far to cause fusion or loss of shape.

9. The duration and rate of heating (p. 526).

10. The size of the pieces of material, as a large piece must be heated for a much longer time than a small one before it shows signs of fusion.

The relation between refractoriness and chemical composition has been described on p. 381. The refractoriness of ceramic materials is only important when they are used at high temperatures, so that it is chiefly of interest in connection with refractory materials.

Fireclay bricks vary greatly in refractoriness, according to the raw material of which they are made. Such bricks are not generally regarded as " refractory " if they have a heat-resistance of less than that of Cone 26 when tested as described on p. 526. The best fireclays have a refractoriness of about Cone 34 (1750° C.), but most first-class fireclay bricks average Cone 31–32 with a minimum of Cone 30, whilst the second-class bricks may have as low a refractoriness as Cone 26. Bricks with a still lower refractoriness should only be employed for purposes where they are not exposed to great heat, so that a high refractoriness is not required.

The Institution of Gas Engineers Standard Specification (1912) requires a refractoriness of not less than Cone 30 for first-class firebricks and not less than Cone 26 for second-class bricks.

The German Admiralty (1913) specifies a refractoriness of Cone 34 for all fireclay bricks in direct contact with glowing coal or oil flames as in recuperators, the sides of boilers and oil furnaces, firebridges, etc., but for brickwork only in contact with flames from coal a refractoriness of only Cone 31 was required, and for work not in direct contact with flame or fuel a refractoriness of Cone 26 is deemed sufficient.

The American Bureau of Standards (1914) requires a refractoriness of not less than Cone 31 (1690° C.) for first-class firebricks and Cone 28 (1630° C.) for second-class bricks.

The American Gas Institute specifies the refractoriness under load for fireclay bricks (p. 180) and not the ordinary refractoriness test.

Fireclay mortar or **cement** is usually made of inferior clay to that used for bricks. The Institute of Gas Engineers requires a refractoriness equal to that of the

bricks used, whilst the German Admiralty (1913) specifies that refractory fireclay mortar must not melt below Cone 34 (1750° C.) and must be hard at Cone 10 (1300° C.).

Grog bricks are generally rather more refractory than ordinary fireclay bricks, as the impurities, being more obvious in the grog than in the raw clay, can be removed before making it into bricks. A small proportion of the alkalies in the clay is usually volatilised during the preparation of the grog, and this further increases the heat-resistance of this material.

Some **refractory porcelain** has a refractoriness of Cone 30–31 (1680° C.), but the glaze begins to soften at about Cone 08*a*–07*a* (950° C.).

Siliceous materials which consist of pure silica fuse at about Cone 35 (1770° C.) if in small pieces, but individual grains of pure silica melt completely at 1470° C. if they are extremely small. Larger pieces of silica, such as bricks, have a much higher fusing-point, and when tested as described on p. 526 have a refractoriness of about Cone 33–35 (1730°–1770° C.).

The best qualities of silica bricks have a refractoriness from Cone 34 to Cone 36 (1750°–1790° C.), but others are much lower, many having a refractoriness not greater than Cones 31–33 (1690°–1730° C.) or even as low as Cone 26 (1580° C.). The Institution of Gas Engineers specifies a refractoriness of Cone 32 (1710° C.) for bricks containing over 92 per cent. of silica and Cone 29 (1650° C.) for bricks containing 80–92 per cent. of silica. K. Endell [1] found that some silica bricks have a refractoriness of 1750° C., and a refractoriness under load of 1650° C.

The American Gas Institute specifies the refractoriness under load for silica bricks (p. 187), and not the ordinary refractoriness test.

Silica bricks can sometimes be used in furnaces in which the contents are at a higher temperature than their nominal refractoriness, as the bricks have so low a thermal conductivity that at a distance of only ½ inch from their hot face their temperature does not exceed about 1500° C., which is well below their softening-point.

The melting-point of tridymite is 1670° C., whilst that of cristobalite is 1625° C.

Fused silica, when tested as described on p. 526, has a refractoriness of 1700°–1800° C., but if heated under pressure or in the form of a long bar or rod supported only at its ends, it may soften sufficiently to lose its shape at 1500° C. Articles made of fused silica should not usually be subjected to prolonged heating at temperatures above 1550° C.

Silica mortar or **cement** should have a refractoriness as nearly as possible equal to that of the bricks with which it is to be used, the difference between them not being greater than 100° C. (five cones). The Institution of Gas Engineers has specified that the cement shall be quite suitable for the purpose of binding the bricks for which it is supplied together and shall be capable of withstanding the same test for refractoriness.

Bauxite bricks are very refractory; when the bauxite is almost pure, the softening point is between Cones 36 and 39 (1790°–1880° C.). As the refractoriness of bauxite bricks increases, their strength decreases, so that the strongest bricks are

[1] *Stahl. u. Eisen,* **41, 6** (1921).

those which contain 20 per cent. or more of silica and a refractoriness corresponding to Cones 33–35 (1730°–1770° C.), which is little, if any, higher than that of silica bricks.

Magnesia bricks made of the purest magnesia with a minimum bond are very refractory and do not soften below Cone 40 (1920° C.), but in order to produce bricks of sufficiently great strength a large proportion of bond is usually employed, and this—being in the nature of a flux—reduces the refractoriness of the bricks.

Chromite bricks are very refractory and generally have a softening-point between 1680° and 1850° C., though some are still more resistant to heat. C. Kanolt found some chromite bricks with a refractoriness of 2050° C. If pure chromic oxide were alone used, the bricks would be practically infusible, but as the cost of the material is too great, a chrome-iron ore of lower refractoriness must be employed. Consequently, the refractoriness of commercial chromite bricks having a clay bond is about 1700° C., whilst that of chromite bricks with a lime bond sometimes exceeds 1850° C.

Carbon bricks are the most refractory materials used in furnace construction, as they do not soften at any temperature reached in industry. They have the disadvantage, however, of slowly burning away if exposed to oxidising conditions, and they are very weak both as regards mechanical strength and in their resistance to abrasion.

Carborundum bricks are more refractory than fireclay, silica, and magnesia bricks, but they cannot be maintained at high temperatures for a long period on account of their decomposition, which commences at temperatures over 2000° C. in the absence of air and at about 1400° C. in an oxidising atmosphere (p. 491). For this reason, their use at very high temperatures is very limited.

Saggers and muffles vary in refractoriness according to the purpose for which they are to be used. Simple refractoriness is not sufficient, as these articles must not lose their shape under load at any temperature likely to be reached when they are in use. Saggers or muffles for burning hard porcelain must have a refractoriness at least equal to that of Cone 35; for bone china, a refractoriness equal to Cone 30 (1570° C.) is sufficient, whilst for inferior ware still less refractory saggers or muffles may be employed. In judging saggers, it is preferable to consider refractoriness under load (p. 184) rather than simple refractoriness, as the loads which saggers often support in a kiln are somewhat stringent.

Glass-melting pots should have a high refractoriness as the conditions under which they are used are very stringent. They should be as refractory as the best quality of material used for firebricks, especially under load (p. 183).

Retorts made of Clay or Grog.—The Institute of Gas Engineers specifies that retorts made of fireclay should not show any signs of fusion at Cone 28 (about 1630° C.); this is approximately equivalent to a refractoriness of Cone 30 (1670° C.) under the test described on p. 526.

Table CXCIII, compiled from the results of various investigators, shows the melting-points of various ceramic materials.

TABLE CXCIII.—*Melting-Points of Ceramic Materials*

Material.	Melting-point or Range, ° C.	Authority.
Kaolin	1735–1740	Kanolt.[1]
Fireclay brick	1555–1725	,,
Alumina	2049	,,
,,	1880	Hempel.[3]
,,	2020	Ruff and Goecke.[2]
,,	2050	Dana and Foote.[7]
Bauxite	1820	Kanolt.[1]
,,	1600–1800	Dana and Foote.[7]
Bauxitic clay	1795	Kanolt.[1]
,, ,,	1800	Dana and Foote.[7]
Bauxite brick	1565–1785	Kanolt.[1]
Alundum cement	1750–2000	Dana and Foote.[7]
Corundum	1950	Kanolt.[1]
Chromium oxide	1990	,,
,, ,,	2059	Ruff and Goecke.[2]
Chromite	2180	Dana and Foote.[7]
Chromite brick	2050	Kanolt.[1]
Magnesia	2800	,,
,,	2250	Hempel.[3]
,,	1910	Goodwin and Mailey.[4]
,,	2000	Lampen.[5]
,,	2050–2100	Saunders.[6]
,,	2150	Dana and Foote.[7]
Magnesia brick	2165	Kanolt.[1]
Quartz	1750	Dana and Foote.[7]
Silica sand	1700–1750	,,
Silica brick	1700–1750	Kanolt.[1]
Lime (pure)	2570	Dana and Foote.[7]
Carborundum	2500	..
Beryllium oxide	2200	..
Cerium oxide	1950	..
Lanthanum oxide	1840	..
Tantalum pentoxide	1875	..
Thoria	2470	..
Titanium oxide	1350	..
Yttria	2400	..
Zircon	2550	..
Zirconia	2700	..

[1] *Trans. Amer. Cer. Soc.*, **15**, 171 (1913).
[2] *Zeit. f. angew. Ch.*, **31**, 1459 (1911).
[3] *Ber. Inter. Kongress angew. Chem.*, **1**, 715 (1903).
[4] *Phys. Rev.*, **23**, 22 (1906).
[5] *J. Amer. Chem. Soc.*, **28**, 846 (1906).
[6] *Trans. Amer. Electro-Chem. Soc.*, **19**, 333 (1911).
[7] *Chem. and Met., Eng.*, **22**, 63, 1920.

The melting-points of the various minerals likely to occur in ceramic materials is shown in Table CXCIV, compiled from the results of various investigators.

TABLE CXCIV.—*Melting-Points of Minerals*

Mineral.	Melting-point or Range, ° C.	Authority.
Albite	1200	Day and others.
Alumina	2050	..
Andalusite	1370	..
Anorthite	1532	Day and others.
Apatite	1270–1300	..
Asbestos	1285–1310	..
Augite	1145–1150	..
Barium metasilicate	1490	R. C. Wallace.
Barium metaborate	1050	Gurther.
Barium orthoborate	1350	,,
Barium pyroborate	1000	,,
Beryl	1410–1430	..
Beryllium metasilicate	2000	..
Beryllium orthosilicate	2000	..
Beryllium oxide	2525	..
Biotite	1155–1240	..
Bronzite	1310–1370	..
Calcium aluminate	1378	Day and others.
Calcium biborate	1025	Gurther.
Calcium metaborate	1095	,,
Calcium pyroborate	1215	,,
Calcium phosphate	1550	O. Nielson.
Calcium orthosilicate (α)	2130	Day and others.
Calcium metasilicate (α)	1540	Hermann.
Tricalcium aluminate	1537	Day and others.
Tricalcium ferrite	1455	Hilpert and Kohlmeyer.
Chromite	1850	..
Corundum	1750–1800	..
Cryolite	977	Pascal.
Diopside	1391	Day and others.
Enstatite	1380–1400	..
Epidote	1250	..
Fayalite	1050–1075	..
Ferrous oxide	1419	Ruff.
Ferrous metasilicate	1100	Grum Grzmailo.
Ferric oxide	1548	Ruff.

TABLE CXCIV—*Continued.*

Mineral.	Melting-point or Range, ° C.	Authority.
Fluorite	1361	Pascal.
Forsterite	1460	Hermann.
Galena	1115	..
Gehlenite	1280–1300	..
Grossular	1150–1250	..
Hornblende	1180–1220	..
Labradorite	1477	Day and others.
Lepidolite	925–945	..
Leucite	1320–1370	..
Magnesium metasilicate	1565	..
Magnesium orthosilicate	1900	..
Magnetite	1538	Ruff.
Monticellite	1435	Hermann.
Muscovite	1255–1290	..
Nepheline	1223	Ginsberg.
Nephite	1180–1210	..
Olivine	over 1600	P. Lebedew.
Orthoclase	1200	Dittler.
Potassium metaborate	947	Van Klooster.
Rhodonite	1210	P. Lebedew.
Scapolite	1120–1140	..
Sillimanite	1816	Day and others.
Sodium metaborate	960	Van Klooster.
Sodium metasilicate	1018	R. C. Wallace.
Spinel	1360	..
Spodumene	1380	..
Strontium metasilicate	1287	..
Strontium orthosilicate	1593	..
Titanite	1200–1300	..
Titanium oxide	1610	Rieke.
Titanium orthosilicate	1650	,,
Tourmaline	1000–1100	..
Wollastonite	1250–1300	..
Zinc metasilicate	1479	..
Zinc orthosilicate	1484	..

From the foregoing it will be seen that the effect of heat on ceramic materials is by no means simple. Much is known of its effects in several directions, but on the whole there is a lamentable lack of exact information which can only be supplied by a large number of experiments and prolonged research.

CHAPTER XIV

ELECTRICAL AND MAGNETIC PROPERTIES OF CERAMIC MATERIALS

The electrical and magnetic properties of ceramic materials are important in connection with both their manufacture and uses. During the manufacture of ceramic materials—particularly those made of clay—the electrical properties of the colloids present are very important (see Chapter VI). Thus, Blake, Morscher, and Swarte have proposed to use the electrical conductivity of raw clays as an aid to their purification, but though the process they suggested has not been very satisfactory, Schwerin's electro-osmose process (p. 289) is being used for this purpose, especially in Germany, and has attracted much attention in this country.

The magnetic properties of various substances—particularly metallic iron—which occur as undesirable impurities in ceramic materials are often important, as they afford a simple means whereby such impurities may be removed. In the use of ceramic materials their electrical conductivity is chiefly important in connection with furnaces, etc., which are heated electrically and in insulators, which are widely used in different forms of electrical apparatus. In both cases, the electrical properties of principal interest to the reader are the electrical conductivity and its converse the electrical resistivity of ceramic wares.

Electrical Conductivity and Resistivity of Ceramic Materials

The electrical conductivity and resistivity of ceramic materials are expressed in different ways according to convenience :—

1. The *electrical conductivity* may be expressed directly in C.G.S. units as *mho* or reciprocal units per cubic centimetre.

2. The *electrical resistance* may also be expressed in C.G.S. units as *ohms* per cubic centimetre (the temperature being also stated both in this and the electrical conductivity).

3. The *puncture voltage*, or the voltage at which a piece of the material of definite thickness is unable to act as an insulator, and, therefore, allows the electric current to pass through it. This is also referred to as the dielectric strength. According to H. F. Howarth, there is no direct relation between the specific ohmic resistance and the puncture voltage.

4. The "*Te*" *value* or the temperature at which the electrical resistance is reduced to 1 megohm per c.c.

5. The *specific inductive capacity* or the relative dielectric strength of the article or material, that of an equal thickness of air being taken as unity.

The general factors influencing the electrical conductivity and resistivity of ceramic materials are :—

1. The composition of the material.
2. The size of the article or test-piece at the time.
3. The density and texture of the material.
4. The manner of heating and the extent to which the material has been heated during the "burning" of the ware.
5. The piezo-electric effect.
6. The temperature of the ware.
7. The length of exposure to the electric current.

The *composition* of the ceramic material largely determines its electrical properties, some materials being much better conductors than others. In composite materials, such as porcelain, the chemical composition is usually important only in so far as it modifies the structure, compositions giving a dense vitreous mass being usually better insulators than those which produce semi-vitreous or porous wares.

TABLE CXCV.—*Electrical Conductivity of Various Minerals*

Good Conductors.	Moderate Conductors.	Bad Conductors.	
Magnetite.	Ferriferous amphiboles and pyroxenes.	Siderite.	Apatite.
Titaniferous magnetite.	Biotite.	Xenotime.	Andalusite.
Magnetic hæmatite.	Tourmaline.	Epidote.	Sillimanite.
Pyrrhotite.	Titanite.	Olivine.	Fluorite.
Chromite.	Rutile.	Staurolite.	Diamond.
Ilmenite.	Anatase.	Garnet.	Topaz.
Hæmatite.	Brookite.	Monazite.	Spinel.
Wolframite.	Cassiterite.	Gypsum.	Cyanite.
Spinel.		Quartz.	Corundum.
Ferriferous cassiterite.		Chalcedony.	Celestite.
Tantalite.		Felspars.	Zircon.
Iron pyrites.		Calcite.	Sandstone.
Chalcopyrite.		Dolomite.	Granite.
		Cordierite.	Porphyry.
		Barytes.	Schist.
		Phlogopite.	Fluorspar.
		Muscovite.	Silicates.
		Tremolite.	Clays.

Table CXCV shows the electrical conductivity of various materials used in the ceramic industries or liable to occur as impurities in ceramic materials.

The *size of the article* is often important with respect to its insulating power, as, according to B. S. Radcliffe,[1] the dielectric strength of porcelains and other ceramic insulating materials is directly proportional to their thickness.

The *density* of a ceramic material is important, as A. S. Watts [2] has proved that the dielectric strength of porcelain and similar materials increases with their density, and, consequently, vitrified articles have a greater dielectric strength than those which are porous.

The *heat-treatment* of the ware during manufacture does not, according to B. S. Radcliffe,[1] affect its dielectric strength, provided such treatment does not cause the formation of blebs, cracks, or other flaws. If, however, any of these defects are produced the resistivity may be greatly diminished. This is in opposition to Bleininger and Riddle,[3] who consider that the rate of cooling has an important influence on the " Te " value of porcelain, as rapid cooling tends to produce a closer and more vitreous structure than slow cooling. Moreover, according to these investigators, the " Te " value of porcelain increases with the maturing temperature, so that the electrical resistance at high temperatures varies inversely with the felspar content, though in a very irregular manner, as shown in Table CXCVI.

TABLE CXCVI.—*Variation of Resistance with Felspar Content*

Per cent., Felspar.	Maturing Temperature, Seger Cone.	" Te " Value.
16	16	560
18	15	390
20	14	440
28	14 ($\frac{1}{2}$ over)	370
30	13	450

According to A. S. Watts,[2] porcelains have a smaller resistance to puncture by electric currents when under- or over-fired than when it is correctly burned, the least resistance being offered by seriously under-fired materials. The vesicular structure produced by over-firing gives a weak material, but if the vesicles are small and not too numerous, so that the mass as a whole is dense and glassy, the puncture-voltage may be very high. Watts gives the following figures as typical of correctly fired porcelains :—

[1] *Trans. Amer. Cer. Soc.*, **14**, 575 (1912).
[2] *Ibid.*, **9**, 615 (1907).
[3] *Loc. cit.*, p. 574.

TABLE CXCVII.—*Puncture Voltage of Porcelain*

	Voltage per 1/100 in.
Porcelains maturing at Cone 6 . .	424
,, ,, ,, 9 . .	426
,, ,, ,, 12 . .	395

The *piezo-electric effect*, in which an electric current is produced by pressure, sometimes seriously reduces the electrical resistance of an insulator if the latter is under compression. Some specimens of quartz and porcelain exhibit this phenomenon, especially in the case of quartz crystals, when the pressure is applied to two diametrically opposite faces parallel to the major axes; a potential difference is then set up in the faces perpendicular to those in which the pressure is applied, this difference varying directly as the pressure. The converse of this may also occur when some quartz crystals are subjected to the prolonged action of an electric current and a change in the dimensions of the crystals may then result. If these changes are hampered by the surrounding magma, great local stresses may occur; consequently, when a piece of porcelain is placed in an alternating field of electrostatic force, a vibratory movement results, owing to the repeated changes in the dimensions of quartz or other crystals similarly affected, and these vibrations may cause a rupture along the cleavage planes of the crystals and also between the crystals and the matrix. The rupture may result in a leakage of current through the spaces so formed, and the dielectric strength then rapidly deteriorates. The piezo-electric effect appears to be exhibited only in connection with certain crystals; it is, therefore, at a minimum in porcelains in which the quartz crystals originally present in the raw materials have been most completely dissolved in the felspathic ground mass by prolonged heating at a suitable temperature. So far as can be ascertained, sillimanite crystals—which are also formed in most well-burned porcelains—do not show this effect.

The *temperature of the ware* when in use has a notable effect on the electrical resistance or insulating power, as most ceramic materials become much better conductors of electricity when at a high temperature than when cold. This is well shown on pp. 614–615.

The *duration of exposure to an electric current* has a noteworthy effect on the apparent resistivity or dielectric strength of porcelains, as a much lower voltage applied for a long time will puncture the material in the same manner as a current of high voltage applied only for a very short time. In making comparative tests it is, therefore, important to state the time during which the current was applied.

Clays.—The electrical conductivity of raw clay is usually regarded as fairly constant, but that of burned clay varies considerably according to the extent of the burning, the changes which have taken place during that process, and the

temperature of testing. Thus, according to Hartmann, Sullivan, and Allen,[1] the resistivity of fireclay bricks at different temperatures is as follows :—

TABLE CXCVIII.—*Electrical Resistivity of Fireclay Bricks*

Temperature.	Electrical Resistivity.	Temperature.	Electrical Resistivity.
° C.	ohms per c.c.	° C.	ohms per c.c.
Cold	Less than 137,000,000	1200	Less than 4,160
800	,, 57,600	1300	,, 2,460
900	,, 20,600	1400	,, 1,420
1000	,, 10,800	1500	,, 890
1100	,, 6,590		

Porcelain.—The electrical insulating power of porcelain and stoneware depends largely on the texture and density, and these are controlled by the chemical composition and the manner of burning. Porcelains high in quartz have a low resistance, because of the piezo-electric effect described on p. 611 ; when the quartz is replaced by sillimanite or clay, the dielectric strength increases. Porcelains high in quartz also tend to be more porous than those richer in fluxes, and, consequently, have a lower dielectric strength.

According to Bleininger and Riddle,[2] the replacement of quartz by kaolin increases the " Te " value of a porcelain, but the use of ball clay reduces the electrical resistance. Fused alumina notably increases the " Te " value, as also does artificial sillimanite, provided it is not in large crystals.

According to B. S. Radcliffe,[3] high-grade fireclays mixed with felspar produce materials with as high a dielectric strength as potash porcelains vitrifying at the same temperature. Ceramic wares in which lime is used as flux instead of potash felspar have, according to B. S. Radcliffe, a lower dielectric strength. Thus, a body containing 6–8 per cent. of lime having the same porosity, burned at about the same temperature as a felspar-porcelain, was found to have only about half the dielectric strength of the latter. B. S. Radcliffe also found that porcelains made with soda-felspar have a greater dielectric strength than those made with potash felspar, though Minneman considers the difference to be too slight to be of importance, provided the porcelain is well vitrified.

According to Bleininger and Riddle,[2] when magnesia is used as a flux in porcelain it increases the " Te " value in an irregular manner, probably as a result of the increased formation of sillimanite. Bleininger and Riddle have also found that when beryllium oxide replaces felspar in a porcelain, it increases the electrical resistance and " Te " values as shown in Table CXCIX.

[1] *J. Amer. Electrochem. Soc.*, **38**, 279 (1920).
[2] *Loc. cit.*, p. 574.
[3] *Loc. cit.*, p. 610.

TABLE CXCIX.—*Effect of Beryllia on "Te" Value*

Beryllium Oxide.	Clay.	Flint.	Maturing Temperature.	"Te" Value.
Per cent.	Per cent.	Per cent.	Seger Cone.	
25	50	25	12	624
35	50	15	11	784
45	50	5	11	798

The proportion of flux in a porcelain also affects its electrical resistance. Thus, according to Gilchrist and Klinefelter,[1] when the felspar content is high the dielectric strength varies directly with the proportion of felspar present, but when the felspar is low the dielectric strength varies directly with the clay-content. It also varies inversely with increases of flint or china clay and increases rapidly with the maximum temperature attained in firing. These investigators found that the greatest dielectric strength is obtained with a porcelain containing a high percentage of felspar and a low percentage of flint, whilst the lowest strength in a porcelain is with a low percentage of felspar and a high percentage of flint.

Weimer and Dun [2] found that (i) at high temperatures porcelains high in felspar have a lower dielectric strength than those which have less felspar, probably on account of the former softening more readily ; (ii) the addition of clay at the expense of flint increases the dielectric strength. Purdy and Potts,[3] however, consider the highest dielectric strength is obtained with a porcelain containing 25–35 per cent. of felspar and not less than 40 per cent. of clay.

The following figures may be regarded as typical of the porcelains investigated, but porcelains vary so greatly that no figures of general application can be given.

At ordinary temperatures, H. F. Haworth [4] has found the specific electrical resistance of the porcelain he examined to be as follows :—

TABLE CC.—*Specific Resistance of Porcelain*

Temperature, ° C.	Specific Resistance, ohms per c.c.	Temperature, ° C.	Specific Resistance, ohms per c.c.
1·63	$143{\cdot}0\times10^{12}$	17·00	$50{\cdot}8\times10^{12}$
2·10	$141{\cdot}0\times10^{12}$	18·65	$42{\cdot}3\times10^{12}$
16·40	$51{\cdot}5\times10^{12}$	20·50	$35{\cdot}5\times10^{12}$

The puncture voltage of porcelain at 25° C. is, according to G. Weimer and C. T. Dun,[2] 64,500–67,500 volts for a thickness of 0·15 inch. It is not generally less than 70,000 volts for pieces $\frac{1}{4}$ inch thick and 100,000 volts for pieces $\frac{1}{2}$ inch thick. E. Rosenthal has stated that the puncture voltage of Berlin porcelain 0·1 inch thick

[1] *Elec. J.*, **15**, 77 (1918).
[2] *Trans. Amer. Cer. Soc.*, **14**, 280 (1912).
[3] *Loc. cit.*, p. 573.
[4] *Proc. Roy. Soc., Series A.*, **81**, A. 547.

is 40,000 volts. The dielectric constant of Berlin porcelain, according to H. Starke, is 5·73 megohms per c.c. That of Seger porcelain is 6·61, and that of statuary porcelain (Parian ware) is 6·84 megohms per c.c.

If the porcelain is heated, its dielectric strength—like that of quartz, mica, hornblende, quartz-glass, and ordinary glass—decreases as the temperature rises. With a rise in temperature of only 100° C. the reduction in the dielectric strength is considerable, and with a rise of 300° C. porcelain becomes only a very poor insulator. This is still further shown in Tables CCI, CCII, CCIII, CCIV, and CCV.

TABLE CCI.—*The Electrical Conductivity of Berlin Porcelain at Different Temperatures*

Temperature, ° C.	Electrical Conductivity.	Authority.
50	$0{\cdot}465\times10^{-15}$	Foussereau.
70	$0{\cdot}25\times10^{-13}$	Dietrich.[1]
160	$0{\cdot}582\times10^{-12}$	
189	$0{\cdot}26\times10^{-11}$	
400	$0{\cdot}05\times10^{-6}$	Goodwin and Mayley.[2]
600	$0{\cdot}6\times10^{-6}$	Pirani and Siemans.[3]
727	$0{\cdot}62\times10^{-6}$	Goodwin and Mayley.[2]
800	$0{\cdot}55\times10^{-6}$	
1000	$1{\cdot}0\times10^{-6}$	
1100	$1{\cdot}3\times10^{-6}$	

TABLE CCII.—*Specific Electrical Resistance at Different Temperatures (H. F. Haworth* [4])

Temperature, ° C.	Specific Resistance, ohms per c.c.	Temperature, ° C.	Specific Resistance, ohms per c.c.
1·63	$143{\cdot}0\times10^{12}$	40·86	$5{\cdot}7\times10^{12}$
2·10	141·0 ,,	43·03	4·85 ,,
16·40	51·5 ,,	47·00	4·01 ,,
17·00	50·8 ,,	50·40	2·64 ,,
18·65	42·3 ,,	54·01	1·78 ,,
20·5	35·5 ,,	56·51	1·44 ,,
27·32	20·0 ,,	58·04	1·11 ,,
30·87	14·0 ,,	59·12	1·08 ,,
34·70	11·8 ,,	62·72	0·77 ,,
37·03	8·24 ,,	64·84	0·64 ,,
40·62	6·25 ,,	81·93	0·15 ,,

[1] *Phys. Zeit.*, **11**, 187 (1910).
[2] *Phys. Rev.*, **27**, 322 (1908).
[3] *Zeit. Electrochem.*, **13**, 969 (1907).
[4] *Loc. cit.*, p. 613.

TABLE CCIII.—*Decrease of Dielectric Strength of Porcelain when Heated (Henderson and Weiner* [1])

(*The average thickness of the test-pieces was* 0·21 *in.*)

Temperature, ° F.	Puncture Voltage.
70	47,500 Tested in oil.
190	44,000 ,,
240	42,700 ,,
75	60,700 Tested in electric furnace.
125	60,100 ,, ,,
175	57,300 ,, ,,
225	42,500 ,, ,,
275	30,250 ,, ,,
325	19,750 ,, ,,
375	10,500 ,, ,,
425	4,000 ,, ,,
475	2,500 ,, ,,
525	2,000 ,, ,,

TABLE CCIV.—*The Puncture Voltage of Porcelain at Temperatures up to* 300° *C. (G. Weimer and C. T. Dun* [2])

(*The test-pieces were* 0·15 *in. thick*)

Temperature, ° C.	Puncture Voltage.	Temperature, ° C.	Puncture Voltage.
25	64,500–67,500	175	39,000–41,000
50	64,250–67,000	200	26,500–29,500
75	63,000–66,500	225	15,000–22,000
100	62,000–63,500	250	7,500–15,000
125	57,000–60,000	275	4,500–11,500
150	49,500–52,500	300	3,000– 7,000

TABLE CCV.—"*Te*" *Value of Ceramic Insulators (F. B. Silsbee and R. K. Honaman* [3]).

Material.	"Te" Value, ° C.	Material.	"Te" Value, ° C.
Fused silica . .	890	Aviation porcelain .	650
Best porcelain . .	790	Automobile porcelain.	490
Mica plug. . .	720		

[1] *Trans. Amer. Cer. Soc.*, **13**, 469 (1911). [2] *Loc. cit.*, p. 613.

[3] *Nat. Advisory Comm. Aeronautics*, 5th Ann. Rept., 77–89 (1919).

The electrical resistivity of insulators at high temperatures may be calculated from the formula $E \times k$, where E is the observed resistance and k is a constant depending on the shape of the insulator. In cup-shaped insulators,

$$k = \frac{\pi d^2}{4t},$$

where d is the diameter of the bottom and t the thickness of the cup. In the case of tubular insulators,

$$k = \frac{2\pi l}{2{\cdot}30 \log_{10} \frac{R_2}{R_1}},$$

where l is the length of the external conducting band and R_2 and R_1 are respectively the external and internal radii of the insulator.

Silica Bricks.—The electrical conductivity of silica bricks is similar to that of fireclay bricks (p. 612). The electrical resistivity of silica bricks is shown in Table CCVI, due to Hartmann, Sullivan, and Allen.[1] These, however, are unduly different from those of Stansfield, M'Leod, and M'Mahon, as shown in the same table.

TABLE CCVI.—*Electrical Resistivity of Silica Bricks*

Temperature, ° C.	Resistivity (Hartmann, Sullivan, and Allen), ohms per c.c.	Resistivity (Stansfield, M'Leod, and M'Mahon), ohms per c.c.
Cold	Less than 125,000,000	..
800	,, 2,380,000	..
900	,, 765,000	..
1000	,, 300,000	..
1100	,, 126,000	..
1200	,, 62,000	..
1300	,, 30,900	9,700
1400	,, 16,500	2,400
1500	,, 8,420	710
1550	..	22
1565	..	18

Fused silica has electrical insulating properties higher than those of glass and porcelain, as shown in Table CCVII, which tabulates results obtained at the National Physical Laboratory.

[1] *Loc. cit.*, p. 612.

TABLE CCVII.—*Comparative Resistivities*

Fused Silica.		Soda-Lime Glass.		Jena Glass Combustion Tubing.	
Temperature, ° C.	Resistivity, Megohm-cm.	Temperature, ° C.	Resistivity, Megohm-cm.	Temperature, ° C.	Resistivity, Megohm-cm.
15	over 200,000,000	18	500,000	16	over 200,000,000
150	,, 200,000,000	145	100	115	,, 36,000,000
230	,, 20,000,000	..	..	150	,, 18,000,000
250	,, 2,500,000	..	..	750	0·1–0·4
350	,, 30,000	..	..	..	..
450	,, 800	..	..	..	..
800	about 20	..	..	..	..

According to tests by the National Physical Laboratory, silica glass has a specific inductive capacity of 3·5–3·6 and a dielectric strength of over 30,000 volts for a thickness of 1·2 mm., the exact figure not being found on account of a sufficiently high voltage not being available.

Magnesia bricks examined by Hartmann, Sullivan, and Allen, yielded electrical resistivity curves which differed very considerably on heating and cooling, there being a peculiar variation in the heating curves which indicate a probable physical change in the structure of the magnesia between 1000° C. and 1500° C., probably due to the formation of an allotropic form of magnesia, viz. periclase. The electrical resistivity of magnesia bricks, as determined by Hartmann, Sullivan, and Allen,[1] and also by M'Leod and M'Mahon, are shown in Table CCVIII.

TABLE CCVIII.—*Electrical Resistivity of Magnesia Bricks*

Temperature, ° C.	Resistivity (H., S., and A.), ohms per c.c.	Resistivity (M'L. and M'M.), ohms per c.c.
Cold	Less than 137,000,000	..
800	,, 5,000,000	..
900	,, 1,240,000	..
1000	,, 708,000	..
1100	,, 560,000	..
1200	,, 193,000	6,200
1300	,, 67,400	..
1400	,, 22,400	..
1500	,, 2,500	..
1550	..	30

[1] *Loc. cit.*, p. 612.

According to Fr. Patent, 425,977 (1911), a mixture of 1–2 parts of powdered magnesia or alumina, 5 of magnesia, 3–4 of water-glass or other silicate or 3 of quartz, has an electrical resistance at a red heat of 10 megohms per c.c., and is stated to be quite non-conductive at ordinary temperatures.

Zirconia bricks were found by Hartmann, Sullivan, and Allen [1] to yield heating and cooling curves with curious differences between them. They also found that on heating up to 1200° C. the resistivity fell rapidly, but above this temperature it fell slowly, as shown in Table CCIX.

TABLE CCIX.—*Resistivity of Zirconia Bricks when Heated*

Temperature, ° C.	Ohms per c.c.	Temperature, ° C.	Ohms per c.c.
Cold	Less than 134,000,000	1200	Less than 7,710
800	,, 558,000	1300	,, 2,100
900	,, 224,000	1400	,, 968
1000	,, 131,000	1500	,, 412
1100	,, 53,800		

Chromite bricks, according to Hartmann, Sullivan, and Allen,[1] have a low electrical resistivity at all temperatures. Between 1100° and 1200° C. they remain fairly constant, increasing from 1200°–1350° C., and again decreasing between 1300° and 1500° C., as shown in Table CCX. The difference between the results of these observers and those of M'Leod and M'Mahon are shown in the same table.

TABLE CCX.—*Resistivity of Chromite Bricks*

Temperature, ° C.	H., S., and A., ohms per c.c.	M'L. and M'M., ohms per c.c.
Cold	48,000,000	..
800	803	2,800
900	525	..
1000	171	..
1100	78	..
1200	63	..
1300	77	..
1400	85	320
1500	41	..

[1] *Loc. cit.*, p. 612.

Carborundum bricks have the electrical resistivities shown in Table CCXI, due to Hartmann, Sullivan, and Allen.[1]

TABLE CCXI.—*Electrical Resistivity of Carborundum Bricks*

Temperature, ° C.	Carbofrax.		Refrax.
	A.	B.	
Cold	Less than 127,000,000	107,200	106·90
800	,, 835,000	12,550	6·45
900	,, 477,000	8,220	3·75
1000	,, 197,000	7,420	4·11
1100	,, 75,000	6,320	3·11
1200	,, 29,500	4,160	2·45
1300	,, 15,200	2,420	2·05
1400	,, 10,100	1,435	1·74
1500	,, 8,590	745	1·62

Clay slips possess electrical properties which are often important in connection with the purification of these materials and in the production of ware by the casting process. Thus, whilst the electrical conductivity of pure, distilled water is 10^{-6} reciprocal ohms (or *mhos*) at 18° C., the presence of even minute quantities of soluble salts causes large differences in the conductivity. When larger proportions are present, the conductivity does not conform to simple rules, but is dependent on several complex considerations.

The conductivity of electrolytes at different temperatures varies considerably; it may be calculated from the formula :

$$C_t = C_{18}(1 + k(t + 18)),$$

where C_t is the conductivity at any given temperature t in ° C., C_{18} is the conductivity at 18° C., and k is the temperature coefficient. For salts, the temperature coefficient varies from 0·02–0·023 for acids, and for some acid salts it is 0·009–0·016, and for caustic alkalies about 0·02 mhos per c.c.

The electrical conductivity of clay slips depends chiefly on the proportion of soluble salts present in the water. Thus, Bleininger and Kinnison [2] found the results shown in Table CCXII.

The presence of calcium sulphate in solution in clay slips greatly decreases their electrical resistivity. In one case, examined by Bleininger and Kinnison, the presence of 0·072 per cent. in a kaolin slip decreased the resistance from 4440 to 720 ohms per c.c.

[1] *Loc. cit.*, p. 612.
[2] *Trans. Amer. Cer. Soc.*, **15**, 523 (1913).

TABLE CCXII.—*Electrical Resistivity of Slips*

	Soluble Salts, per cent.	Resistance in ohms, reduced to 60° F.
Surface clay, Cleveland . .	2·10	2110
,, ,, Curtice . .	1·05	2160
No. 3 Fireclay, Aultman . .	0·94	3790
Shale, Canton . . .	0·77	3050
Shale, Independence . .	0·60	3970

Determination of Electrical Conductivity, Resistivity, etc.—A rough separation of minerals into good and poor conductors may be rapidly made by a method suggested by T. Crook.[1] The apparatus consists of two copper plates a few inches square, one of which has one surface coated with a layer of shellac, which is continued over the edge of the plate, forming a narrow strip on the opposite surface. The shellac-coated surface of one copper plate is placed next to the uncoated surface of the other, but is separated from it by two pieces of glass coated with shellac. The upper plate is charged electrically by means of an electrophorus consisting of a plate of ebonite, resin, sealing wax or shellac, on a metal base and a circular metal disc of the same diameter with an insulated handle. If the plate of the electrophorus is rubbed with a flannel or piece of fur, a negative charge of electricity is induced in it, so that, on placing the metal disc on its lower surface, it is charged positively and a complementary negative charge is given to the outer surface. This is removed by touching it with the finger. A small quantity of the sample to be examined is placed on the upper side of the lower copper plate of the pair previously mentioned, and the disc to which the insulating handle is attached is placed upon the upper copper plate. The minerals which are good conductors of electricity will immediately adhere to the upper plate and can be removed therefrom, whilst the non-conductors remain on the lower plate. For accurate work, a larger apparatus operated by a more powerful current is preferable, but the simple device just described is often useful.

The electrical resistivity of an article may be determined by passing an electric current through it and measuring the resistance by means of a potentiometer.

The *puncture-voltage* (*i.e.* the voltage required to break down the resistance and allow a current to pass readily) is generally determined by placing a sample of known thickness between two electrodes and applying a gradually increasing voltage until puncture occurs and noting the maximum voltage applied, the test-piece being usually immersed in oil, unless the test is made at a high temperature, when oil cannot, of course, be used.

[1] *Economic Mineralogy* (Longmans, Green & Co.).

Magnetic Properties of Ceramic Materials

Clay, silica, most of the silicates, and many other ceramic materials are non-magnetic, but some of the impurities are susceptible to magnetic attraction, and, consequently, this property is sometimes used in their removal. Table CCXIII shows the magnetic properties of different minerals.

Table CCXIII.—*Magnetic Properties of Minerals*

Highly Magnetic.	Moderately Magnetic.	Feebly Magnetic.	Almost Non-Magnetic.	
Magnetite.	Hypersthene.	Chlorite.	Zircon.	Rutile.
Titanoferite.	Augite.	Staurolite.	Corundum.	Barytes.
Ilmenite.	Garnet.	Epidote.	Galena.	Most iron-free minerals.
Pyrrhotite.	Siderite.	Limonite.	Fluorspar.	
Hæmatite.	Olivine.	Actinolite.	Pyrite.	Clay.
	Hornblende.	Cyanite.	Cassiterite.	Silica.
	Chromite.			

Some burned fireclays are feebly magnetic on account of the presence of magnetic iron oxide or other minerals which are attracted by a magnet. All ferrous silicates are magnetic, and Zirkel found that fused phyllite ($FeOAl_2O_3SiO_2$) is also magnetic.

The magnetic properties of minerals, etc., may readily be determined by means of a small electro-magnet. A convenient one, suggested by T. Crook,[1] consists of two limbs, each 1 inch diameter and 4 inches long, wound with seven layers of 16-gauge wire, each layer having about forty turns. The two adjustable pole-pieces should be $1\frac{1}{4}$ inches wide and $\frac{1}{3}$ inch thick, slotted so as to be moved nearer to, or farther from, each other, and secured by screws to the limbs. An 8-volt battery is quite sufficient for this instrument. In use, the magnet is suspended over a smooth cardboard tray containing the sample to be examined. If desired, the most magnetic particles may be removed with a permanent magnet, and the " moderately magnetic " grains then removed by means of an electro-magnet, with its poles about $\frac{1}{2}$ inch apart. Afterwards, the poles of the magnet may be placed only $\frac{1}{4}$ inch or rather less apart and the " feebly magnetic " minerals may then be separated. The residue may be regarded as practically non-magnetic. Alternatively, the minerals may be suspended in water, forming a slip, which can then be stirred with the magnet until all the magnetic particles have been removed.

Magnets, arranged in series, are extensively used for removing minute particles of metallic iron from clay and body slips, these particles being largely derived from the machines used to grind the clay and other ingredients of the slips.

[1] *Loc. cit.*, p. 620.

CHAPTER XV

OPTICAL PROPERTIES OF CERAMIC MATERIALS

THE optical properties of ceramic materials are important in two ways :

(*a*) As an aid to identifying the various crystals and other substances present in a ceramic material.

(*b*) In order to produce a desired appearance such as a particular colour or lustre, translucency, transparency, etc., in the finished product or ware.

IDENTIFICATION OF CERAMIC MATERIALS BY OPTICAL PROPERTIES

As mentioned in Chapter X, an examination of the optical properties of various materials in a mixture affords a very useful method of determining the amount of some mineral. The examination may be made by means of a hand-lens or, more usually, by means of a microscope. The principal properties which can readily be determined by this means are as follows :

1. The colour, lustre, etc. (see Chapter III).
2. The crystal form (see Chapters I and X).
3. Reflection.
4. The refractive index.
5. The birefringence.
6. The extinction angle.
7. The optical sign.
8. The pleochroism.
9. The interference figures.

Reflection occurs when a ray of light falls on a surface and, instead of being absorbed, much of it is returned from the absorbent surface at the same angle to a line perpendicular to the surface of the material as the entering ray. When the amount of absorption is high, no reflection occurs ; when little absorption occurs, most of the light is reflected and the substance appears to be glossy or shining.

The **refractive index** [1] often affords a convenient method of identifying minerals. All transparent substances have the power of bending or refracting a beam of light passing obliquely through them to a varying degree, according to their nature and density. This property is termed *refraction*, and the amount of refraction is termed the

[1] Care must be taken not to confuse the term "refractive" with the term "refractory" the former relates to light, the latter to heat.

refractive index, which is found from the equation $\mu = \frac{\sin i}{\sin r}$, where i is the angle which the entering ray makes with a line perpendicular to the surface of the substance, r is the angle which the ray passing through the substance makes with the perpendicular, and μ is the refractive index as shown in fig. 51. The refractive index of any substance is constant and is independent of the angle at which the light falls on the substance.

The refractive indices of various minerals found in ceramic materials is shown in Table CCXIV.

TABLE CCXIV.—*Refractive Indices.*

Mineral.	Max.	Min.	Mineral.	Max.	Min.
Anatase	2·489		Hornblende	1·64	1·68
Andalusite	1·643	1·632	Hypersthene	1·705	1·682
Albite	1·534		Kaolinite	1·563	
Andesine	1·558		Labradorite	1·555	
Anorthite	1·582		Lepidolite	1·60	
Apatite	1·638	1·634	Leucite	1·508	
Augite	1·723	1·698	Microcline	1·526	1·519
Barytes	1·647	1·636	Monazite	1·841	1·796
Biotite	1·6	1·56	Muscovite	1·601	1·563
Brookite	2·741	2·583	Nepheline	1·543	
Bytownite	2·74		Oligoclase	1·544	
Calcite	1·658	1·486	Olivine	1·689	1·654
Cassiterite	2·093	1·997	Opal	1·45	
Celestite	1·631	1·622	Orthoclase	1·525	1·519
Chalcedony	1·55		Phlogopite	1·60	
Chromite	Very high		Pyrophyllite	1·57	
Cordierite	1·544	1·535	Quartz	1·553	1·544
Corundum	1·769	1·760	Rutile	2·903	2·616
Cristobalite	1·484		Serpentine	1·57	
Cyanite	1·729	1·717	Sillimanite	1·682	1·660
Diamond	2·42		Sodalite	1·48	
Diopside	1·70		Spinel	1·72	
Dolomite	1·682	1·503	Staurolite	1·746	1·736
Enstatite	1·67	1·66	Strontianite	1·52	
Epidote	1·746	1·714	Titanite	2·008	1·899
Fluorite	1·434		Topaz	1·627	1·618
Garnet	High		Tourmaline	1·64	1·62
Glaucophane	1·639	1·621	Tridymite	1·477	
Gypsum	1·53		Xenotime	1·816	1·721
Halloysite	1·53		Zircon	1·993	1·931
Hæmatite	3·22	2·94			

The refractive index of crystals which are sufficiently large may be found by measuring the relative angles of the entering and emerging rays directly in a refractometer, but for the minute crystals usually found in ceramic materials, other methods must be used, the crystals being viewed through a microscope. A very convenient method devised by Schrœder van der Kolk consists in immersing the coarsely

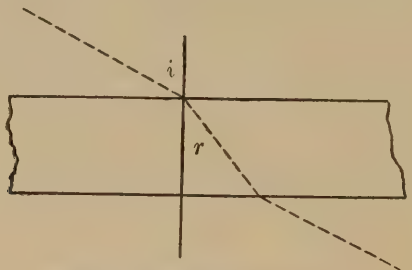


Fig. 51.—Refraction of Light.

powdered mineral on a thin glass slide in various liquids having different, but known, refractive indices. When the mineral has the same refractive index as the liquid in which it is immersed, the grains will be practically invisible, so that by using different liquids one will finally be found of which the refractive index approximates to that of the mineral, and the refractive index of this liquid may be taken as that of the mineral.

Table CCXV, due to Schrœder van der Kolk, shows the refractive indices of various liquids which are useful for this purpose.

Table CCXV.—*Refractive Indices*

Material.	Refractive Index.	Material.	Refractive Index.
Ethylene chloride . .	1·450	Monobrombenzol . .	1·561
Olive oil	1·469	Orthotoluidine . . .	1·571
Benzol	1·501	Aniline	1·583
Cedarwood oil . . .	1·505	Bromoform . . .	1·590
Monochlorbenzol . .	1·523	Cinnamon oil . . .	1·605
Ethylene bromide . .	1·536	Moniodobenzol . . .	1·619
Clove oil	1·544	*a*-Monochlornaphthlene	1·635
Nitrotoluol . . .	1·546	*a*-Monobromnaphthlene .	1·655
Nitrobenzol . . .	1·552	Methylene iodide . .	1·740
Dimethylamine . .	1·558	Sulphur in methylene iodide	1·839

Another ingenious method of determining the refractive index of a substance was devised by Becke, who found that if the particle to be examined is immersed in a

liquid and the objective lens of the microscope is raised until the grain is out of focus, a bright line will move from the material having the lower refractive index to the one having the higher value, so that with any liquid and a given material it is possible to determine readily which has the higher refractive index. By using liquids of different refractive index that of the mineral will eventually be found.

Another useful method consists in tilting the mirror of the microscope so as to cut off part of the light from the field of view and to cast a shadow so that the crystals appear dark on one edge and light on the other. If the dark edge lies on the side of the crystal opposite to the shadow, the crystal has a lower index of refraction than the liquid in which it is immersed, whilst if the dark edge is on the side nearest to the shadow, the mineral has a higher refractive index than the liquid. By using several liquids of known refractive index in succession, the liquid corresponding to the refractive index of the mineral can be found.

A very refined and accurate method, devised by A. B. Dick, is especially valuable for determining the nature of minerals whose refractive indices are very close to each other, as in the case of tridymite and cristobalite (p. 623). In this method, a small quantity of the coarsely powdered sample is immersed in a suitable liquid with a refractive index equal to that of one of the constituents present. When the sample is viewed through a microscope, by means of a dark ground illuminator, using yellow monochromatic light, coloured fringes will be seen around the grains, and these fringes will be of an ultramarine tint if the minerals and the liquid have exactly the same refractive indices. If the liquid has the higher refractive index, the fringes will be paler and brighter and sometimes even white, whilst if the liquid has the lower refractive index, the fringes will be of a red or orange shade. The colour of these fringes thus distinguishes between the particles of higher and lower refractive index and makes it possible to estimate the proportions of grains of different minerals when their refractive indices are very close. For example, in the examination of a mixture of tridymite and cristobalite a solution of mercury-potassium-iodide may be used, as this has, with a monochromatic yellow sodium light, a refractive index of 1·477 which is equal to that of tridymite. Any cristobalite present, having a refractive index of 1·484, will be readily discriminated from the tridymite, the test being extremely delicate.

The use of the refractive index is by far the simplest and most direct method of distinguishing substances of the same chemical composition but different physical properties, such as tridymite and cristobalite, calcite and aragonite, lightly burned magnesia and periclase, etc. It is the most important method for investigating the proportion of unaltered quartz in a silica brick.

Double refraction is produced when a single ray of light entering a substance emerges as two distinct refracted rays, one of which, measured by the fraction $\frac{\sin i}{\sin r}$ is termed the *ordinary ray*, whilst the other is termed the *extraordinary ray*. The difference between these two refractive indices—the *birefringence*—is often used in the identification of minerals. Table CCXVI shows the most important minerals in order of birefringence.

TABLE CCXVI.—*Birefringence of Minerals* (*Milner and Part*)

Uniaxial Positive.		Uniaxial Negative.	
Pennine	·003	Idocrase	·001
Quartz	·009	Apatite	·004
Zircon	·062	Nepheline	·005
Cassiterite	·099	Melilite	·005
Rutile	·287	Corundum	·008
		Tourmaline	·017
		Scapolite	·021
		Cancrinite	·028
		Anatase	·061
		Calcite	·172
		Dolomite	·189
Biaxial Positive.		**Biaxial Negative.**	
Zoisite	·006	Orthoclase	·006
Albite	·008	Microcline	·007
Enstatite	·009	Andesine	·007
Topaz	·009	Oligoclase	·008
Staurolite	·010	Kaolin	·008
Chloritoid	·015	Cordierite	·008
Augite	·021	Labradorite	·008
Sillimanite	·021	Axinite	·009
Diallage	·024	Andalusite	·011
Diopside	·030	Serpentine	·011
Olivine	·036	Anorthite	·012
Sphene	·121	Hypersthene	·013
Brookite	·160	Wollastonite	·014
		Cyanite	·016
		Actinolite	·025
		Tremolite	·028
		Muscovite	·038
		Epidote	·040
		Biotite	·044
		Hornblende	·072
		Aragonite	·156

Polarised light is obtained by passing a ray of ordinary light through two prisms composed of certain minerals (such as tourmaline and iceland spar) [1] placed in such a position relative to each other that they totally reflect or polarise any light projected along their axes, with the result that no light is transmitted through them. If, however, a fragment of certain minerals is placed between the two prisms, an amount of light corresponding to the optical properties of the crystal will be transmitted, but if one of the prisms is rotated on its axis, a position will be reached at which the light is again completely polarised and is extinguished, the field of view becoming quite dark. The angle at which this extinction occurs is termed the *extinction angle*, and is often useful in identifying minerals, particularly plagioclase felspars (see Table CCXVII).

TABLE CCXVII.—*Extinction Angles of Felspars (Milner and Part)*

Felspar.	Extinction Angle measured from the Albite Lamellæ.	Extinction Angle measured from the Long Axes of Microlites.
Albite	6°–16°	10°–20°
Oligoclase	0°–5°	0°– 7°
Oligoclase (basic) . . .	6°–16°	..
Andesine	16°–22°	8°–20°
Labradorite	27°–45°	30°–42°
Bytownite	45°–50°	49°–56°
Anorthite	50° and over.	58°–64°

If a number of flakes of any felspar are examined, two series of approximately similar extinction angles will be obtained, corresponding to the fragments which are split parallel to the two principal faces of the crystal, and from a comparison of these angles with the corresponding ones obtained with known complex felspars, an unknown felspar may be identified. The colours and forms of the minerals viewed by means of polarised light are also characteristic, and are useful in determining their nature.

When the dark field of view produced by the prisms alone remains black, even after a given mineral has been placed between them and continues so at any angle of the polariser, it is said to be *isotropic*. Crystals belonging to the cubic or isometric system are always isotropic (except under abnormal circumstances), and so are transverse sections of tetragonal and hexagonal crystals, but no sections of orthorhombic, monoclinic, or triclinic crystals have this property. Hence, only crystals

[1] These prisms are usually known as "nicols," after their discoverer. For convenience they are usually fitted to a microscope as, by this means, they may be used for examining much smaller particles than would otherwise be possible.

of the three last-named systems, and sometimes those of the tetragonal and hexagonal systems, are visible in polarised light.

Optical Sign.—For the observation of compensation effects and the determination of the optical sign, a quartz wedge and a simple gypsum plate should be kept at hand, as they are extremely useful. The ordinary quartz wedge used in examining sections will, as a rule, be found too feeble, owing to the thickness of the grains. The best form of quartz wedge for use in the optical examination of sand grains is the graduated thick wedge devised by Dr Evans.[1]

Quartz wedges are usually made so that the vibration-direction along the length of the wedge is that of the extraordinary (slow) ray. Such a wedge is called positive, and in reporting results a positive wedge is always assumed to be used. The thicker wedges usually needed for examining small grains should be graduated so that each interval corresponds to 1000 micro-millimetres of relative retardation. Gypsum plates, on the contrary, are usually made so that the direction of the length is the vibration-direction of the fast ray. It matters little which way the quartz wedge or gypsum plate is made, so long as its nature is determined before use. In no case should it be assumed that a quartz wedge is positive, as the maker may, purposely or inadvertently, make it negative.

If one doubly refracting substance is placed above another in such a way that the direction of vibration of the slow ray of one coincides with the direction of vibration of the fast ray of the other, the effect is subtractive, the order of the colours will be lowered, and if the relative retardation of the two substances is the same, the result—if viewed between crossed nicols—will be darkness, as each plate exactly counteracts the other. This is known as the *position of compensation*.

The compensation test consists in placing a small positive crystal (say of zircon) in the position of extinction between crossed nicols, then turning either the nicols or the stage through 45° (*i.e.* into the position of greatest illumination), and insert a positive quartz wedge between the analyser and the objective of the microscope. If the long edge of the wedge lies parallel to the prism edge, and the crystal is thin enough to show a definite interference colour, it will be noticed that the order of the colour increases, indicating that this is the additive position.

If now the crystal or polarising system be turned through 90°, so that the wedge is inserted at right angles to the prism edge, compensation will take place, and the order of the interference colours will get gradually lower until the position of complete compensation is reached, indicating that this is the subtractive position. This fact shows that the vibration-direction of the crystal parallel to the prism edge is that of the slow ray, and since it is also that of the extraordinary ray the crystal must be positive.

If a negative crystal is used (*e.g.* apatite), the compensation takes place with the long edge of the quartz wedge along the prism edge. This simple compensation test is sufficient to show the optical sign of a uniaxial prism.

For biaxial prisms other tests are required to ascertain the optical sign. In all crystals where there is a prismatic cleavage with straight extinction or a low extinction

[1] *Mineralogical Mag.*, **14**, p. 90.

angle, it is useful to apply the compensation test in order to ascertain whether the direction of elongation of the cleavage fragment is that of the fast-ray or slow-ray vibration.

With a biaxial figure the position of the quartz wedge should be noted in relation to the optic axial plane when the wedge is in a compensating position. The biaxial crystal (such as a cleavage plate of mica which is optically negative) should be placed on the stage of the microscope, a gypsum plate being inserted diagonally across the centre so as to produce the characteristic black cross when the nicols are crossed. The stage or the nicols should then be turned through an angle of 45° so as to produce the hyperbolic brushes and to illuminate the centre of the field. The quartz wedge is then inserted and will lie either parallel to or at right angles to the optic axial plane. If it lie along the optic axial plane, addition will result and the colour will rise ; if it lie at right angles to this plane, compensation will take place.

If a positive biaxial mineral is used, the reverse result will be obtained, *i.e.* compensation occurs when the quartz is inserted along the optic axial plane and addition or rise in colour when it is inserted at right angles to this plane.

If compensation takes place when the wedge is inserted at right angles to the optic axial plane, the mineral is negative ; if it occurs when parallel to the optic plane, the crystal is positive.

Optical activity is a property characteristic of certain substances which rotate a ray of polarised light to either the right (dextro-rotatory) or to the left (lævo-rotatory). It has been found that all carbon compounds which possess this property contain an asymmetric atom, *i.e.* one which is united to four different elements or groups of elements. Hitherto, no optical activity has been observed in clay—probably because the crystals are much too small—but both dextro- and lævo-rotatory quartz are known, though their constitution has not been ascertained.

The optical activity of quartz must not be confused with that of some carbon compounds, because there are two classes of optically active substances : (i) those which, like quartz, depend for this power on their crystalline state, that is, on the grouping of the molecules in the crystals ; and (ii) those in which the rotatory power is inherent in each molecule, since it is not affected by solution. It is this molecular rotatory power which is of such great importance in organic chemistry in determining the molecular constitution of complex substances. Unfortunately the optical activity of quartz does not appear, at present, to be of much assistance in determining its constitution.

A property which is very useful in identifying some minerals is that termed **pleochroism**, and is due to the fact that some crystals absorb light unequally in different directions, and so when viewed from one angle they have a different colour from that when they are viewed from another angle. In most cases, the absorption of light is only for certain colours, only the residual colour being transmitted, but sometimes almost the whole of the light is absorbed. Thus, biotite varies from a light brown in one direction to deep brown or nearly black in another. The various colours may readily be seen by rotating the prism placed below the stage of the microscope (*i.e.* the polariser), but without using the upper prism (*i.e.* the analyser),

and watching the mineral during the rotation. If preferred, the mineral may be rotated. The following minerals which occur in ceramic materials are :—

Intensely pleochroic . . .	Biotite. Cyanite (if coloured). Epidote. Hornblende. Hypersthene. Tourmaline.
Moderately pleochroic . .	Chlorite. Corundum (if coloured). Sphene.
Slightly pleochroic . . .	Some augites.

Minerals are termed *dichroic* or *trichroic* according to the number of colours visible when the substance is viewed in the direction of its various crystalline axes.

Isotropic crystals belonging to the cubic or isometric system are never pleochroic. Coloured uniaxial crystals belonging to the tetragonal and hexagonal systems are dichroic, whilst coloured biaxial crystals belonging to the orthorhombic, monoclinic, or triclinic systems are trichroic.

Interference.—If two waves of light of the same wave-length and amplitude, and travelling in the same direction, meet crest to crest, and trough to trough, the result is to give the particles affected by the wave double amplitude. If, however, the waves meet crest to trough and trough to crest, the particles are motionless, and the waves are said to *interfere* and extinguish one another. If ordinary white light is used, the waves overlap by interference and the colours of the spectrum are seen. Unless the light is first passed through a very narrow slit the edges of the colours will be blurred instead of sharply distinguished.

It is impossible to deal fully with the effect of light in passing through minerals in the present volume ; further information will be found in the standard text-books on mineralogy and petrology. A particularly useful summary of the optical properties of minerals occurring in ceramic materials will be found in *An Introduction to Sedimentary Petrography*, by H. B. Milner (Murby & Co.). Some of the commoner properties of the various minerals found in ceramic materials are mentioned in the descriptions of the various minerals in Chapter X., and these properties, in conjunction with the other tests mentioned in that Chapter, will generally enable the more usual minerals to be identified. The use of *X-ray spectra* for this purpose has been described on p. 322.

Ultramicroscopic particles are so minute that they are invisible when viewed through a microscope of the usual type, even though it be of the highest power. Their movements may, however, be observed by suspending the particles in a suitable fluid, such as water, and passing a powerful beam of light horizontally through the liquid. If the latter were perfectly clear it would, when viewed through a microscope, appear to be black and void, but if any particles are present in suspension they are

illuminated by the light and present the appearance of bright globules, resembling the motes in a sunbeam. A combination of a microscope with a device for illuminating in the manner just described is known as an *ultramicroscope* (fig. 52). By its use the movement of particles (but not their shape) may be examined even when the particles are as small as 0·0000004–0·0000006 mm., and as these dimensions approach

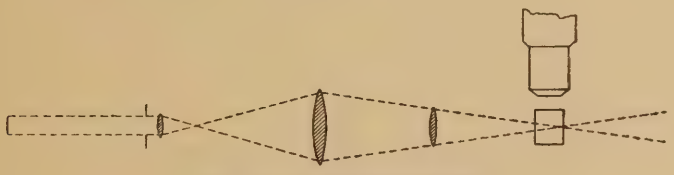


FIG. 52.—ULTRAMICROSCOPE.

the molecular dimensions of complex compounds, the ultramicroscope affords considerable scope for investigation of the behaviour of such molecules.

The ultramicroscope is particularly valuable in the examination of clays, as these are among the most minute particles found in the ceramic materials, and by its aid the Brownian movement (p. 242), characteristic of colloids, has been observed in many clays.

OPTICAL PROPERTIES OF MANUFACTURED CERAMIC ARTICLES

The principal optical properties of ceramic articles in the manufactured state are :—

1. *Colour* and *lustre*, which are dealt with in Chapter III.
2. *Transparency*, as in the case of silica-glass.
3. *Translucency*, in connection with fused silica, porcelain, china-ware, etc.
4. *X-ray spectrum.*

Transparency is so well known a term that it needs no description. The most transparent solid is glass, which is not usually regarded as a ceramic material, except in some parts of the United States. The most transparent substance which is generally regarded as a ceramic material is fused silica, quartz glass, or silica glass.

Transparency is obtained by the use of the purest materials and prolonged heating after complete fusion. Any cloudiness in a substance which is normally transparent is usually due either to impure materials or to imperfect fusion.

As silica-glass is the only completely transparent ceramic material, it is the only one possessing such optical properties as refractive index, dispersive power, etc., but individual particles present in other ceramic materials possess them even when the mass as a whole may appear to be opaque. The principal optical properties of silica glass are shown in Table CCXVIII.

Opacity is the converse of transparency and is the property of a substance which prevents it allowing any light to pass through it. Opaque substances may be examined under the microscope with direct or reflected light by shielding the light from the

mirror below the microscope stage and illuminating the substance by means of direct light or by reflecting light on to it by means of a white card held above it.

TABLE CCXVIII.—*Optical Properties of Silica Glass*

Refractive index .	1·45848	Dispersive power .	0·01472
Refracting power .	0·45848	Recriprocal relative dispersion . .	67·92
Mean dispersion. .	0·00675		

Translucency is a very desirable property in porcelain and china-ware used for domestic purposes. It is intermediate between transparency and opacity, so that whilst a translucent substance will allow some light to pass through it, the shape of solid objects cannot readily be distinguished through it. Translucency is chiefly due to the formation of so large a proportion of clear transparent fused material that the ware becomes semi-transparent or translucent. It depends chiefly upon the following factors :—

1. The chemical composition.
2. The manner and duration of firing the ware.
3. The extent of crystallisation.
4. The shape, and particularly the thickness, of the sample.

The *chemical composition* has a very important influence on the translucency of ware, as it determines the amount of transparent glassy material which can be produced and, therefore, the chemical composition may be said to control the translucency. For the same reason, the nature of the siliceous material present may have a marked effect, especially as silica from different sources does not always produce the same translucency. Thus, according to Steger,[1] sand and geyserite, when substituted for Norwegian quartz in porcelain, decrease the translucency of the ware.

Fluxes increase the translucency of wares. H. E. Ashley [2] measured the thickness of ware and of various compositions through which the light from a 16 candle-power electric light or a Welsbach gas-burner was visible and found that the addition of 3 per cent. of fluorspar to a white-ware body increased the thickness from 1·65 mm. to 2·4 mm. The addition of 0·4 per cent. of whiting had about the same effect, whilst 3 per cent. of whiting only increased the thickness to 2·0 mm.

Gilchrist and Klinefelter [3] found that, in general, the translucency of porcelains is increased in proportion to the felspar and inversely to that of the clay present. The kind of clay used also has a great influence on the translucency, ball clays affording a greater translucency than china clay, but tending to spoil the colour of the ware. The use of talc in porcelain increases the translucency.

The *manner and duration of firing* should be such as to secure the maximum

[1] *Ber. der Deut. Keram. Gesellschaft*, **3**, Part II, 50–3 (1922).
[2] *Trans. Amer. Cer. Soc.*, **8**, 150 (1906).
[3] *Elec. J.*, **15**, 77 (1918).

amount of vitrification if translucent ware is required, because, as explained on p. 632, the translucency depends on the proportion of " glassy " matter. That the temperature attained in the firing and the duration of the firing can increase the glassy matter is clear from what has been stated in Chapter XIII. Moreover, it is well known that raising the temperature or prolonging the firing will make the ware more translucent, some mixtures which are opaque at Cone 7 (1230° C.) being very translucent at Cones 10–12 (1300°–1350° C.).

E. Roth [1] found that the translucency of porcelains rich in sodium and potassium silicates increases up to Cone 12 (1350° C.), remains constant from Cones 12–14 (1350°–1410° C.), and again increases above Cone 14 (1410° C.) on account of the solution of quartz by the molten material at or near 1400° C.

The *extent of crystallisation* which occurs in ceramic ware to some extent depends on the burning process. It is found that the larger the proportion of sillimanite present, the greater is the translucency of the ware, because the lathlike sillimanite crystals form a felted mass or skeleton which enables a larger proportion of fused or vitrified matter to be present without the ware losing its shape. It should be clearly understood that the translucency is primarily due to the glassy or vitrified ware and not to the crystals ; the latter are merely a form of reinforcement.

The *thickness of the sample* or article obviously affects the translucency, as no ceramic wares are wholly transparent, like glass. W. Steger [2] has found that the translucency of porcelain is inversely proportional to its thickness and that the translucency increases as the proportion of clay decreases, the ratio of translucency : clay in any given porcelain being constant for all thicknesses.

Translucency may be measured in various ways, though these do not give results comparable with each other. As translucency is generally regarded as the extent that light can pass through a substance, the simplest measure of translucency would appear to be the intensity of the light which can just be seen through the ware. Hence, Priest,[3] and others have, independently, suggested measuring the translucency by means of a photometer. To obtain comparative results two lights of equal and standard intensity must be employed. These lights are placed on opposite sides of the piece to be examined and are moved backwards and forwards until the light which has passed through the ware is of the same intensity as that which shines directly on to the surface of the ware.

Parmelee and Lawrence [4] measure the translucency by allowing ultraviolet rays to pass through the test-piece on to a sensitive photo-electric cell, which thereupon produces an electric current of an intensity corresponding to that of the light passing through the test-piece. The potential of the current as measured by a galvanometer is, therefore, proportional to the translucency. The photo-electric cell consists of a vessel filled with argon and silvered internally, having a thin film of potassium deposited on the silver to form the cathode of an electric circuit and a loop of platinum

[1] *Sprech.*, **55**, 533–34 (1923).
[2] *Ber. Deut. Ker. Ges.*, **2**, 63 (1921).
[3] *Trans. Amer. Cer. Soc.*, **17**, 150 (1915).
[4] *J. Amer. Cer. Soc.*, **6**, 630 (1923).

wire to form the anode. An ultraviolet ray falling on the potassium surface causes it to become electrically charged, and the ions then liberated pass to the anode and so cause a definite deflection of the galvanometer.

Another method of measuring translucency is that of R. H. Hursh,[1] which consists in determining the smallest mesh of gauze which can be seen through the sample by placing it in contact with the gauze and illuminating the latter by an incandescent electric light of known candle-power placed at a distance of 3 inches behind the gauze and measuring the thickness of the sample. By this test, the best porcelain with a thickness of 1·1 mm. has a translucency equivalent to the use of a 20–40-mesh gauze ; the same porcelain 3 mm. thick has a translucency corresponding to the use of an 8–10-mesh gauze.

[1] *Trans. Amer. Cer. Soc.*, **13**, 103 (1911).

INDEX

α-Alumina, 339.
α-β Change in quartz, 328.
Abrasion, effect of porosity on, 73.
  effect of texture on, 38.
  resistance of bauxite bricks to, 132.
    of bricks to, 128.
    of carbon bricks to, 133.
    of chrome bricks to, 133.
    of earthenware to, 133.
    of floor tiles to, 130.
    of glazed ware to, 133.
    of magnesia to, 132.
    of refractory bricks to, 130.
    of refractory materials to, when hot, 131.
    of silica to, 132.
    of zirconia bricks to, 133.
  resistance to, 124, 125.
    testing, 134.
Abrasive tests, 134.
Abscissæ of graphs, 455.
Absolute scale of temperature, 533.
Absorption, determination of, 81.
  effect of porosity on, 72.
    of size of pores on, 71.
  of heat, 519.
Absorptive power of colloidal gels, 235.
  of dry clay, 75.
  of plastic clay, 76.
α-cristobalite, nature of, 328.
  specific gravity of, 216.
Accrington bricks, strength of, 173.
Acid defined, 316, 318.
  radicle, defined, 317.
  salt, defined, 320.
  water in silicates, 338.
Acids and bases, product of reaction of, 434.
  effect of, on clay, 243.
    on clay paste, 275.
    on osmotic pressure of colloids, 233.
  removal from solution by clay, 241.
Ackermann, A. S. E., 126, 273, 274.
Actinolite, birefringence of, 626.
  magnetic properties of, 621.
Action of heat on colloidal gels, 235.
  selective, *see* Selective action.
Activity and temperature, 322.
Adamantine, lustre of, 95.
Adhesion, limit of, 268.
Adhesive bond, 153.
Adsorption, 235.
  v. lattice structure, 324.
  by clays, 238, 242.
  by colloidal gels, 235.
  characteristic equation for, 236.
  electro-, 230.
  of gases and vapours, 238.
  of liquids by clay, 239.
  of solids by clay, 239.
    from solution by clay, 240.
  selective, by clay, 240.
Affinity, *see* Chemical affinity.
  constants of reactions, 449.
  different, 442.
  disposing, 442.
After-expansion of silica bricks, 568, 569.
Agate, 424.
Ageing, 274.
  effect of, on strength, 156.
    of, on water required, 269.
Aggregate, effect of, on strength, 160.
Aggregates, nature of, 2.
Aggregation, effect of, on plasticity, 261.
  states of, 14.
Air, importance of, in burning clays, etc., 546.
  thermal conductivity of, 587.
  -separation, 53.
Akermanite, 482.
  latent heat of fusion of, 601.
  melting-point of, 601.
Alabama, graphite in, 23.
Albite, 342.
  -anorthite phase diagram, 457.
  birefringence of, 626.
  effect of fusion of, on specific gravity, 211.
  formation of, 480.
  isomorphism in, 334.
  melting-point of, 606.
  -orthoclase-anorthite phase diagram, 463.
  properties of, 416.
  refractive index of, 623.

Alcohol, effect of clay on, 238.
Aleksiejeff, 261.
Alexander, 242.
Algæ, a cause of colour, 97.
Alkali defined, 320.
effect of, on clays, 242, 248, 275.
on osmotic pressure of colloids, 233.
on silica glass, 505.
on silicates, 505.
in chemical analyses, 360.
in clay, 364.
volatilisation of, 551.
Alkaline glazes, 383.
silicates, 364.
Allen, 468, 612, 616, 617, 618, 619.
B. J., 249, 284.
Allophane, 20, 345, 412.
structure of, 7.
thermal curve of, 352.
water in, 423.
Allotropic changes, effect of size of grains on, 31.
on cooling, 560.
on heating, 545.
forms of silica, 327.
Alteration of structure, 25.
Alum as bond in silica bricks, 399.
Alumina, 339.
affinity of fluxes for, 315.
artificial, structure of, 14.
as base or acid, 322.
-barium oxide-silica system, 481.
-base ratio, 479.
-base-silica system, 474, 478.
colloidal, 251.
combined water in, 340.
constitution of, 339.
decolorising effect of, 101.
effect of, on colour of clay wares, 101.
on expansion of glazes, 579.
on porosity, 68.
on silica bricks, 497.
on titanic oxide, 368.
free, in clays, 364.
occurrence of, 426.
fused, 403.
constancy in volume of, 570.
garnets, 342.
heat of formation of, 531.
hydrous, decomposition of, by heat, 545.
in calcined clay, 351.
raw clays, 364.
-iron oxide system, 471.
-lime-silica system, 478.
-lime system, 470, 471.
-magnesia system, 471.
-silica system, 481.
melting-point of, 605, 606.
molecular heat of, 598.
Alumina *continued*—
polymerisation of, 350, 351.
polymerising temperature of, 339.
-potash-silica system, 480.
replacement of, by other oxides, 335, 389.
-silica eutectic, 472.
ratio in clays, 371.
in glazes, 386.
system, 472.
-soda-silica system, 480.
specific gravity of, 221.
heat of, 598.
use of, in glazes, 385.
-zinc-silica system, 482.
Aluminates, 322, 356, 421.
in clays, 415, 421.
Aluminium, effect of, on silica glass, 498.
hydroxides, types of, 339.
graphic formula for, 308.
minerals in clays, 421.
Alumino-silicates, 364, 367.
as cementing materials, 16.
chemical constitution of, 325, 340, 341.
corrosiveness of, 441.
effect of sulphuric acid on, 504.
ferric, 495.
in chromite, 430.
in clay, 415.
thermal curves of, 349, 352.
viscosity of, 441.
-silicic acids, classification of, 342.
anhydrides, 342.
Aluminous bricks, materials used for, 402.
strength of, 191.
materials, hardness of, 126.
shrinkage of, 570.
minerals, impurities in, 427.
occurrence of, 426.
Alundum cements, melting range of, 605.
coefficient of expansion of, 581.
specific gravity of, 221.
strength of, 191.
α-magnesia, 220, 356.
American Ceramic Society, 197, 219, 522.
Foundryman's Association, method of comparing texture, 57.
Gas Institute, 180, 187, 373, 400, 602, 603.
hard porcelain, strength of, 178.
National Brick Manufacturers' Association, 197.
Society for Municipal Improvements, 128, 176.
for Testing Materials, 76, 82, 174, 175, 196, 197, 201, 500, 501, 523.
Standard sieves, 45, 47.
Ammonium carbonate, use of, in purifying clay, 288.
hydrate, effect of, on silica glass, 505.

Amorphous carbon, 358.
definition of, 5.
magnesite, structure of, 8.
materials, effect of heat on, 8.
silica, 328, 329.
occurrence of, 424.
use of, 425.
solids, 487.
substances, defined, 487.
nature of, 5.
Amphiboles, 416.
Amphoteric electrolytes, effect of, on clay, 243.
Analcime, 341, 342.
formation of clay from, 354.
Analcite, *see* Analcime.
Analyses, typical, misuse of, 314.
Analysis, chemical, 359.
interpretation of, 360.
mechanical, 44, 49.
of clay, after calcination, 410.
rational, 409.
recalculated, 410.
Anatase, 429.
birefringence of, 626.
crystalline form of, 4.
electrical conductivity of, 609.
in clay, 421.
refractive index of, 623.
Andalusite, 342, 413, 480.
birefringence of, 626.
crystalline form of, 4.
electrical conductivity of, 609.
formation of clay from, 354.
melting-point of, 606.
refractive index of, 623.
thermal curve of, 352.
Andesine, 417.
birefringence of, 626.
refractive index of, 623.
Ångstrom units, 323.
Angular grains, 27.
Anhydride defined, 317.
Ankerite, as a cementing material, 15.
Annealing, 559.
Anorthite, 342, 367, 416, 478.
-albite-orthoclase phase diagram, 463.
phase diagram, 457.
birefringence of, 626.
-bytownite, formation of, 440.
crystallisation of, 461.
latent heat of fusion of, 601.
melting-point of, 601, 606.
refractive index of, 623.
Anorthoclase, formation of clay from, 354.
Anthophyllite, 416.
structure of, 25.
Apatite, 421, 422.
action of hydrochloric acid on, 503.
Apatite *continued*—
birefringence of, 626.
electrical conductivity of, 609.
in clay, 422.
melting range of, 606.
refractive index of, 623.
Apparent density, 203, 205.
of various ceramic materials and articles, 212–223; see also under their various names.
porosity, 62.
determination of, 81.
Apparent specific gravity, 203.
determination of, 221, 224.
effect of heat on, 208.
α-quartz, 328.
specific gravity of, 216.
heat of, 597.
Aragonite, 367, 420.
birefringence of, 626.
replacement of, by quartz, 5.
Aron, 20, 102.
Arrested reactions, 487.
Arrhenius, 240, 245.
Arsenic oxide as opacifier, 395.
Artificial colours, producing, 115.
Arzuni, 334.
Asahara, 358.
Asbestos, bricks, porosity of, 79.
crystalline form of, 4.
" fuel," 25.
melting range of, 606.
specific gravity of, 220.
structure of, 25.
thermal resistivity of, 594.
Asch, W. & D., 237, 309, 327, 332, 337, 338, 339, 340, 343, 346, 347, 348, 350, 351, 352, 353.
Ashes, a source of scum, 121.
Ashley, H. E., 199, 240, 245, 248, 251, 265, 267, 278, 350, 567, 632.
Association of particles, 445.
Aston, F. W., 299.
Atmosphere during firing, importance of, 554.
in kiln, effect of, on colour, 118.
in kiln, effect of, on shrinkage, 566.
in kiln, effect of, on strength, 162.
of furnace, effect of, 502.
reducing, in kiln, a cause of discoloration, 121.
Atomic compounds, 302.
heat, definition of, 512.
of various materials, 513.
number, 301.
structure, 301.
of amorphous substances, 322.
volume of basic elements in glazes, 384, 385.
weights, 303.
list of, 303.

Atoms, 300.
cubic arrangement of, 324.
mobility of, 437, 438.
structure of, 301.
α-tridymite, 328.
specific gravity of, 216.
Atterberg, 260, 268, 269, 282.
number, 268.
Attraction, molecular, effect of, on plasticity, 261.
Augite, 342, 415, 459.
birefringence of, 626.
magnetic properties of, 621.
melting range of, 606.
pleochroism of, 630.
refractive index of, 623.
Austin, 163.
Aventurine glazes, 398.
Avogadros number, 234.
Axinite, birefringence of, 626.
Aylesbury sand, texture of, 42.
Aylesford red bricks, strength of, 173.
Ayrshire bauxitic clay, coefficient of expansion of, 571.
specific gravity of, 213.

β-Alumina, 339.
Back reaction, 449.
Bacteria, effect of, on clay, 275.
Baddeleyite, 429.
colour of, 120.
hardness of, 126.
Bagshot clays, colour of, when burned, 109.
Baking *v.* burning, 557.
Balanced reaction, 451.
Ball clays, 414.
binding power of, 284.
blue, 108.
Brownian movement in, 242.
burned, colour of, 109.
carbonaceous matter in, 422.
casting, 284.
cause of colour of, 106.
coefficient of expansion of, 571, 573.
colloidal matter in, 263.
colour of, 95, 107.
composition of, 372.
dry, strength of, 159, 171, 172.
effect of, on electrical resistance, 612.
iron sulphides in, 419.
ivory, 108.
size of grains in, 34.
translucency afforded by, 632.
water required to develop plasticity of, 269.
Baraboo quartzite bricks, specific gravity of, 219.
Barium carbonate as a cementing material, 15.
as a scum preventor, 97.
effect of, on silica glass, 505.
compounds, 368.
felspar, 417.
metaborate, melting-point of, 606.
metasilicate, melting-point of, 606.
minerals in clays, 421.
orthoborate, melting-point of, 606.
oxide-alumina-silica system, 481.
effect of, on expansion of glazes, 579.
on shrinkage, 567.
heat of formation of, 531.
in glazes, 387.
in porcelain, 377.
-lime-silica system, 474.
-lithia-silica system, 477.
-silica system, 469.
-soda-silica system, 477.
pyroborate, melting-point of, 606.
silicate, 421, 477.
sulphate, 421.
as bond in silica bricks, 399.
reaction of, with soda, 451.
Barratt, 235.
Barringer, 391.
Barus, 486, 597.
Barysilite, 333.
Barytes, 421.
as a cementing material, 15.
electrical conductivity of, 609.
refractive index of, 623.
replacement of, by hæmatite, 5.
Base-alumina ratio, 479.
-silica system, 474, 478.
-base-silica systems, 474.
Bases and acids, product of reaction of, 434.
defined, 316, 319.
effect of, on clay, 243.
on fusing-point, 387.
in glazes, 386.
reaction of, with silica, 505.
removal of, from solution by clay, 241.
soluble, to be fritted, 387.
Basic materials, effect of, on silicates, 466.
effect of sulphuric acid on, 504.
silicates, 332.
slag, corrosive action of, 496.
Bastard ganister, Scottish, texture of, 40.
Bath bricks, finishing temperature of, 553.
Bauer, 518, 588, 590, 592, 596.
Baugh, 244, 247.
Bauschinger, 134.
Bauxite, 339, 402, 427.
action of hydrochloric acid on, 503.
bricks, 402, 499.
and spalling, 584.
effect of lime on, 499.

Bauxite bricks *continued*—
effect of slag on, 499.
firing, 556.
temperature of, 558.
hardness of, 132.
hot, strength of, 165.
melting range of, 605.
permeability of, 90.
porosity of, 80.
refractoriness of, 603.
resistance of, to abrasion, 130, 131.
to slags, 500.
to sudden changes of temperature, 583.
shrinkage of, 569.
strength of, 190.
texture of, 43.
thermal conductivity of, 593.
effect of burning temperature on, 585.
colour of, 97, 119.
combined water in, 340.
constitutional formula of, 340.
decomposition of, by heat, 490, 545.
dehydrated, 339.
effect of heat on, 340.
fused, coefficient of expansion of, 581.
hardness of, 126.
in clay, 421.
melting range of, 605.
nodular structure of, 25.
shrinkage of, 570.
specific gravity of, 221.
structure of, 19.
Bauxitic clay, coefficient of expansion of, 571.
melting-point of, 605.
fireclays, 421.
Bayeux porcelain, coefficient of expansion of, 576, 577, 578.
β-cristobalite, 328.
specific gravity of, 216.
Beading, 386.
Becke, 624.
Beckenkamp, J., 326, 327, 328.
Bedford, T. G., 578.
Beecher, M. F., 153, 181.
Beilby, Sir G., 274.
Bell, M. L., 130, 134, 169, 187, 206.
Bencke, A., 240.
Bending temperature, 165.
Bentonite, 264, 412.
Berdel, E., 393.
Berkshire, red-burning clays of, 109.
Berlin porcelain, 375, 378.
coefficient of expansion of, 574, 576, 577, 578.
dielectric strength of, 614.
Berthelot's law, 530.
Bertrand, L., 364.
Beryl, melting range of, 606.
Beryllium metasilicate, melting-point of, 606.
orthosilicate, melting-point of, 606.
oxide, effect of, on electrical resistance, 612.
melting-point of, 605, 606.
source of, 21.
spinel, graphic formula of, 356.
Berzelius, 341.
Biedermann, 260.
Bigot, A., 79, 340.
Bijvoet, J. M., 357.
Bilz, 230.
Binary silicates, 466.
systems in ceramics, 466.
Binding agent, 507.
changes in, during burning, 547.
particles of aggregate, 507.
power, 141.
and plasticity, 281.
of clay, 281.
measuring, 202, 282.
Bingham, 272.
Binns, C. F., 241, 389, 396.
Biotite, 342, 417.
as catalyst, 443.
birefringence of, 626.
electrical conductivity of, 609.
formation of, 440.
melting range of, 606.
pleochroism of, 629, 630.
refractive index of, 623.
Birefringence, 411, 625.
Bischof, 279, 381, 382.
Biscuit ware, colour of, 112.
discoloration of, 121.
finishing temperature of, 553.
porosity of, 80.
producing, 554.
Bisilicates, 332.
effect of, on basic materials, 466.
Bismuth oxide in crystalline glazes, 397.
Bisque, *see* Biscuit ware.
Bitter spar, 427.
Black articles, production of, 102, 105, 116.
bricks, 111.
core in clays, 423.
hearts, production of, 423.
spots, causes of, 121.
tiles, 111.
Blackening of lead glazes, 555.
Blake, 260, 265, 608.
Blasberg, 497.
Blast furnace bricks, permeability of, 90.
furnaces, resistance of, to abrasion, 125.
bricks for, porosity of, 77.
Bleininger, A. V., 67, 74, 145, 149, 153, 171, 177, 179, 180, 183, 195, 207, 210, 213, 270, 277, 288, 292, 331, 364, 373, 443, 482, 574, 595, 610, 612, 619.

Blistering, 392.
Blisters in articles, 22.
Bloated ware, 369.
Bloating, 161, 562, 565.
Blocks, hollow, porosity of, 77.
large, importance of porosity in, 75.
susceptibility to sudden changes in temperature, 582.
texture of, 38.
Blotches, due to pyrites, 103.
in crystals, 3.
in firebricks, 115.
Blount, 225.
Blows, effect of, in reducing strength, 169.
Blue articles, production of, 102.
ball clays, 108.
bricks, 111.
apparent density of, 214.
bond in, 148.
cause of colour of, 103.
of strength of, 148.
finishing temperature of, 555.
porosity of, 76.
strength of, 173, 174.
colour, effect of impurities on, 105.
produced by iron compounds, 97.
producing, 116.
discolorations, cause of, 121.
glazes, 395.
tiles, 111.
Blueing clays, cause of, 104.
Blumenthal, G., Jun., 133, 136.
Blunging, 60.
β-magnesia, 356.
Bodies, composition of, 382.
raw, identified by colour, 106.
Bodin, V., 165, 179, 180, 188, 189, 190, 191, 192, 195, 548.
Body-centred cube lattice, 323.
Boeck, P. A., 5, 21, 573, 581.
Boernstein, 594, 595.
Bogitch, B., 41, 127, 135, 145, 186, 190, 225, 329, 581.
Boilers, corrosive action of flue-dust on, 496.
Boiling, 561.
point, 523, 528.
Bole, 413.
Bole, G. A., 263.
Bond, adhesive, 153.
clays, dry, strength of, 171, 172.
effect of, on porosity, 68.
on strength, 147, 160.
hydraulic, 154.
in silica bricks, corrosion of, 498.
plastic, 153.
power of the, 153.
proportion of, 18.
vitrified, 154.
Bonds for silica bricks, 399.
Bone, W. A., 238.
china ware, 112; see also China-ware.
Boric acid as catalyst, 443.
oxide, effect of, on expansion of glazes, 579.
in glazes, 388, 389.
Born, M., 513.
Bornite, 420.
Boswell, P. G. H., 42, 48.
Boswell's grading graph, 57, 58.
Bottiger, 246.
Bottom Busty fireclay seam, effect of weathering on, 255.
Boudouard, 468.
Boulder clay, structure of, 21.
Bourry, 270.
Bowen, N. L., 481.
Boys, C. V., 252.
β-quartz, 328.
specific gravity of, 216.
heat of, 597.
Bradshaw, L., 132, 135, 157, 186, 595, 596.
Braesco, 329.
Bragg, W. H., 8, 11, 19, 259, 265, 307, 322, 327, 334, 358.
W. L., 327.
Bravais, 323, 325.
Brearley's sentinel pyrometers, 540.
Breunnerite, 427.
colour of, 97, 120.
texture of, 43.
true specific gravity of, 220.
Brick clays, apparent density of, 212.
composition of, 374.
felspar in, 417.
texture of, 34.
water required to develop plasticity of, 269.
earths, burned, colour of, 109.
colour of, 108.
Bricks, American, strength of, 174.
Brinell hardness of, 127, 128.
clay, structure of, 17.
cracking of, caused by lime, 374.
crushing strength of, 173.
crystals in, 323.
effect of burning on, 438.
of frost on, 73.
of repeated heating on, 163.
of shape of grains in, 29.
finishing temperatures for, 555.
from colliery refuse, 370.
made of paste, 9.
minerals in, 415.
modulus of rupture of, 176.
porosity of, 76.
testing, 82.
resistance of, to abrasion, 128, 130.

Bricks *continued*—
resistant to acid open-hearth and heating furnace slags, 497.
steamed, effect of frost on, 74.
strength of, suggested minima for, 174.
texture of clay for, 37.
transverse strength of, 175.
See also under their various names.
Brickwork, apparent density of, 213.
strength of, 172.
Bridgeman, 325.
Briggs, T. R., 230.
Brindled bricks, apparent density of, 214.
Brinell ball test, 135.
hardness of bricks, 127, 128.
of raw clay, 126.
Briquetting ores, reactions in, 505.
Bristol stoneware glaze, 392.
British Standard sieves, 45, 46.
Thermal Unit, 509.
Thompson-Houston Company, 379, 498.
Brittleness, 141.
due to overheating, 562.
explained, 139.
Brody, E., 513.
Bronzite, 415.
melting range of, 606.
Brookite, 429.
birefringence of, 626.
crystalline form of, 4.
electrical conductivity of, 609.
hardness of, 126.
in clay, 421.
refractive index of, 623.
Brown, G. H., 149, 176, 179, 189, 288, 292, 364, 373, 501, 590.
colours produced by iron compounds, 97.
production of, 117.
discolorations, cause of, 121.
goods, producing, 115.
magnesite, cause of, 120.
scum, 123.
Brownian movement, 11, 54, 232, 242.
β-tridymite, 328.
specific gravity of, 216.
B.T.U., 509.
Bubbles in crystals, 3.
Buckner, O. S., 159, 161.
Buddington, 482.
Building bricks, American, strength of, 174, 175.
finishing temperature of, 553.
German, strength of, 175.
hardness of, 127.
permeability of, 89, 90.
porosity of, 76, 80.
resistance of, to weathering, 166.
specific gravity of, 215.
strength of, 172, 174.
Building bricks *continued*—
thermal conductivity of, 587, 593.
resistivity of, 594.
volume-weight of, 215.
Buff burning clays, 114.
colour, cause of, 99.
coloured goods, producing, 114.
Bulk specific gravity, 203.
Bull dog, corrosive action of, 496.
Bunting, E. N., 85, 86.
Bunzli, 483.
Burchartz, H., 77, 215.
Burned clay, constitution of, 348.
clays, colour of, 108.
hardness of, 127.
iron compounds in, 420.
mineralogical nature of, 412, 415.
specific gravity of, 213.
siliceous materials, minerals in, 426.
Burner's skill exemplified, 440.
Burning carbonates, 490.
cement produced by, 16.
ceramic materials, 544.
clays, 544.
effects of heat in, 544.
effect of, on colour, 105.
on strength, 159.
the temperature on thermal conductivity, 590.
formation of glassy material in, 558.
manner and duration of, 632.
period, 163.
phase conditions in, 466.
temperature, effect of, on porosity, 69, 70.
on thermal conductivity, 585.
Burt, 389.
Burton, 231.
Bytownite, 417.
refractive index of, 623.

Calcareous cement in rocks, 15.
clays, vitrification range of, 553.
sandstone, bond in, 18.
Calcined china clay, action of hydrochloric acid on, 503.
clay, adsorbing power of, 238.
constitution of, 348.
magnesia, 428.
practically insoluble, 503.
Calcining, alteration of structure by, 26.
furnaces, porosity of bricks for, 78.
Calcite, 367, 420.
action of hydrochloric acid on, 503.
as a cementing material, 15.
birefringence of, 626.
crystalline form of, 4.
distinction of, from aragonite, 625.

Calcite *continued*—
electrical conductivity of, 609.
hardness of, 126.
refractive index of, 623.
replacement of, by hæmatite, 5.
by quartz, 5.
space-lattice of, 324.
Calcium aluminates, 421.
hydraulic properties of, 503.
in matte glazes, 396.
melting-points of, 470, 606.
alumino-silicates, 367.
in matte glazes, 396.
biborate, melting-point of, 601, 606.
borate, latent heat of fusion of, 601.
Calcium carbonate, 367.
as a cementing material, 15.
conditions of equilibrium of, 453.
decomposition of, by heat, 367, 433, 447, 451, 490.
heat of formation of, 531.
occurrence of, 428.
chloride as bond in silica bricks, 399.
compounds in clays, 367, 420.
mineralogical nature of, 428.
felspars, 417.
ferrates, 421, 503.
hydroxide, effect of, on strength of fired clays, 155.
metaborate, melting-point of, 606.
metaferrate, 471.
metasilicate, 333, 467, 478.
forms of, 468.
melting-point of, 606.
minerals in clay, 420.
orthoferrate, 471.
orthosilicate, 333, 467, 468.
melting-point of, 606.
oxide, see Lime.
phosphate, 367, 421.
melting-point of, 606.
pyroborate, melting-point of, 606.
silicates, 367, 421, 434, 476, 479.
and lithia, 476.
formation of, 462, 468.
fusing-point of, 467.
hydraulic properties of, 503.
in phase diagram, 475.
sulphate, 367, 369, 421.
and sodium carbonate, interaction of, 436.
as bond in silica bricks, 399.
effect of heat on, 367.
heat of formation of, 531.
in clay slips, effect of, on electrical resistivity, 619.
in glazes, 387.
occurrence of, 428.
spoils slip, 285.
Calculation of molecular formulæ, 312.
Caldwell, D. R., 241.
Callendar, 327.
Calorie, 509.
Calorimeters, 508, 510.
Calorites, 540.
Cambridge & Paul Instrument Co., Ltd., 537.
Campbell, 356, 503.
Cancrinite, birefringence of, 626.
Capillary structure, 24.
of clay particles, effect of, 76.
tube, flow of water in, 87.
Caramel, effect of, on plasticity, 275.
Carbide bricks, burning, 557.
shrinkage of, 570.
crucibles, 404.
Carbides, 404.
and carboxides, impurities in, 430.
constitution of, 357.
crystalline structure of, 2.
decomposition of, 491.
effect of, on magnesia bricks, 498.
hardness of, 126.
structure of, 14.
use of, 430.
Carbofrax, effect of rapid cooling on, 584.
Carbon, affinity of, for oxygen, 493.
allotropy of, 358.
amorphous, 358.
bricks, 404, 604.
burning, 557.
hot, strength of, under load, 179.
inertness of, 500.
resistance of, to temperature changes, 583.
specific gravity of, 596.
heat of, 596, 599.
strength of, 189.
structure of, 19.
thermal conductivity of, 588.
colour of, 119.
compounds, commercial nature of, 430.
deposition of, on fireclay bricks, 169.
heat of formation of, 531.
effect of, on magnesia bricks, 498.
on strength, 169.
heat evolved on burning, 530.
mineralogical nature of, 430.
monoxide, decomposition of, by red-hot clay, 238, 443.
by fireclay bricks, 497.
heat evolved on burning, 530.
heat of formation of, 531.
oxidation of, 493.
retardation of oxidation of, 493.
specific gravity of, 221.
thermal resistivity of, 594.
Carbonaceous matter as a source of colour, 106.
decomposition of, by heat, 491, 545.

Carbonaceous matter *continued*—
effect of, on colour, 105.
in burning clays, 423.
on texture, 370.
in clay, 370, 422, 430.
occurrence of, 430.
removal of, 491.
use of, to increase porosity, 65.
Carbonated water, action of, on carbonates and silicates, 504.
Carbonates as cementing materials, 15.
burning, 490.
decomposition of, by heat, 490, 545.
Carbonic acid, action of, on carbonates and silicates, 504.
Carborundum, 430.
analyses of, 405.
bricks and spalling, 584.
burning, 557.
effect of molten iron on, 500.
of silica on, 500.
of slags on, 500.
electrical resistivity of, 619.
hardness of, 133.
hot, resistance of, to abrasion, 131.
permeability of, 90.
porosity of, 80.
refractoriness of, 604.
resistance of, to abrasion, 130, 133.
to temperature changes, 583.
strength of, 191.
structure of, 17.
texture of, 44.
thermal conductivity of, 592, 593.
resistivity of, 594.
colour of, 119.
composition of, 404.
constitution of, 357.
crystalline structure of, 14.
decomposition of, 491.
decrease in strength of, when hot, 165.
effect of hydrofluoric acid on, 504.
of soda on, 500.
lustre of, 95.
melting-point of, 605.
space lattice of, 324.
specific gravity of, 221.
thermal conductivity of, 586, 592.
Carboxide bricks, 404.
Carboxides, 357.
crystalline structure of, 2.
hardness of, 126.
inertness of, 500.
use of, 430.
Carlow, chert beds at, 506.
Carlsson, F., 149, 363, 364, 366.
Carnalite, 413.
Cassiterite, 422.
Cassiterite *continued*—
birefringence of, 626.
electrical conductivity of, 609.
refractive index of, 623.
space lattice of, 324.
Casting, deflocculants for, 285, 286.
electrolytes for, 285.
process, 283.
slips, 10, 283.
temperature of, 287.
water in slips for, 285, 286.
Catalysis, 443.
Catalysts, 443.
action of, 444.
effect of, 442.
Catalytic action, 442.
of clay, 238.
of fireclay, 73.
agent, effect of, 238.
Caustic magnesia, soluble in water, 503.
soda, use of, in purifying clay, 288.
Cavities in crystals, 3.
Celestite, 421.
electrical conductivity of, 609.
refractive index of, 623.
Cellular materials, 23.
structure, 23.
production of, 23.
substances, 7.
Cellulose, as a bond, 153.
Celsian felspar, 417, 342.
Celsius grade of temperature, 509, 533.
Cement, 507.
calcareous, in rocks, 15.
effect of, on zirconia bricks, 500.
ferruginous, in rocks, 15.
a result of weathering, 507.
in plastic materials, 19.
in sandstone, 18.
Portland, as a bond, 154.
precipitation of, in rocks, 15.
production of, in burning, 16.
silica, 15.
Cementation, 507.
Cementing materials in rocks, 15.
Cements, alumino-silicate, 16.
for silica bricks, 498.
glassy, 16.
in finished goods, 16.
siliceous, porosity of, 79.
texture of, 44.
Centigrade and Fahrenheit scales, 534.
scale of temperature, 533.
unit, 509.
Centres of crystallisation, effect of, 489.
Ceramic materials defined, 1.
properties of, see under their various names.

Cerium, effect of, on silica glass, 498.
oxide, melting-point of, 605.
source of, 21.
Ceylon, baddeleyite in, 120, 403.
graphite in, 23, 404.
Chabazite, 342.
Chain compounds, 308.
formulæ, 343.
Chalcedony, 253, 424.
as a cementing material, 15.
colloidal nature of, 7, 13.
colour of, 119.
effect of repeated heating on, 218.
electrical conductivity of, 609.
refractive index of, 623.
specific gravity of, 216.
Chalcopyrite, 420, 507.
electrical conductivity of, 609.
Chalfont St Peters, bricks made at, 373.
Chalk, 367, 374.
flint, specific gravity of, 216.
Chalybite, 420.
as a cementing material, 15.
Change, electrical, on particles, 228.
Changes due to water in natural minerals, 253.
during vitrification, 552.
effected by weathering, 253.
in physical properties effected by heat, 528.
state caused by heat, 523.
effected by water, 227.
in temperature, 519.
in volume caused by heat, 520.
of state, 444.
Chapman, 325.
Chapney, 118.
Checker bricks, permeability of, 90.
porosity of, 80.
thermal conductivity of, 593.
resistivity of, 594.
Chemical action, 432.
and physical changes, 433.
avoidance of, 432.
effect of light on, 444.
of pressure on, 440.
of temperature on, 445.
of vapour pressure on, 440.
prevention of, 432.
rate of, 446.
resistance to, and porosity, 76.
types of, 435.
in weathering, 506.
affinity, 433.
analysis, 359.
interpretation of, 360.
changes, cause of, 433.
during vitrification, 552.
in cooling, 559.
combination, laws of, 302.
Chemical *continued*—
composition, 146.
effect of, on coefficient of expansion, 573.
on strength, 146.
compound defined, 299.
compounds, definite, 462.
constitution, effect of, on true specific gravity, 209.
of ceramic materials, 299; see also Constitution.
equations, 316.
formulæ, 306.
furnaces, porosity of bricks for, 78.
notation, 306.
porcelain, strength of, 178.
reaction and porosity, 446.
velocity of, 448, 449, 450.
of increasing, 450.
reactions and time, 439.
factors influencing, 437.
occurrence of, 435.
occurring at high temperatures, 490.
tendency of, 435.
rearrangement, 436.
systems, phase conditions in, 452.
ware, permeability of, 90.
Chert, 424, 506.
colour of, 119.
Chiastolite, 342.
China clay, 414.
apparent density of, 206.
birefringence of, 411.
Brownian movement in, 242.
calcined, action of hydrochloric acid on, 503.
colour of, 109.
capillary structure of, 24.
clay-substance from, 344.
colloidal matter in, 263.
colour of, 107.
composition of, 372.
crystalline nature of, 11, 411.
structure of, 19.
effect of heat on density of, 206.
on porosity, 68.
-felspar mixtures, effect of heat on, 66.
heating curve of, 349.
index of refraction of, 411.
interference figure of, 411.
kaolinite in, 20.
mica in, 20.
molecule, 347.
organic matter in, 422.
polarisation colours of, 411.
purification of, 288.
quartz in, 20.
size of grains in, 33.
tourmaline in, 20, 107.

China clay *continued*—
translucency afforded by, 632.
of, measuring, 634.
true specific gravity of, 210.
vitrification range of, 553.
water required to develop plasticity of, 269.
X-ray spectrum of, 11, 19.
-ware, 112.
apparent density of, 214.
burning, 554.
cause of discoloration in, 121.
clays for, 375.
hardness of, 133.
porosity of, 80.
strength of, 177, 199.
Chinese porcelain, 376, 377, 378.
sea-green glaze, 394.
Chipping, resistance of china-ware to, 199.
Chlorides, a source of scum, 122.
Chlorinated atmosphere, effect of, 118.
Chlorite, 342, 418.
action of hydrochloric acid on, 503.
as cementing material, 15.
magnetic properties of, 621.
pleochroism of, 630.
Chloritoid, birefringence of, 626.
Chocolate colour, production of, 118.
Chorlton, 589.
Chrome bricks, see Chromite bricks.
ores, mineralogical composition of, 429.
use of, 429.
-tin pinks, 395.
Chromite, 404.
bricks, 404.
and spalling, 584.
burning, 557.
electrical resistivity of, 618.
fusing temperature of, 558.
hot, strength of, 165.
inertness of, 500.
melting range of, 605.
permeability of, 90.
porosity of, 80.
refractoriness of, 604.
resistance of, to abrasion, 130, 131, 133.
to temperature changes, 583.
shrinkage of, 570.
specific gravity of, 221.
strength of, 150, 181, 189.
structure of, 17.
thermal conductivity of, 592, 593.
of effect of burning temperature on, 585.
resistivity of, 594.
transverse strength of, at high temperatures, 181.
composition of, 404.
crystalline form of, 4.
electrical conductivity of, 609.
Chromite *continued*—
hardness of, 126.
impurities in, 430.
magnetic properties of, 621.
melting-point of, 605, 606.
occurrence of, 429.
permeability of, 90.
polymerisation of, 358.
porosity of, 80.
refractive index of, 623.
sand, 20.
segregation of, 25.
shrinkage of, 358.
Chromium compounds, colour depends on atmosphere in kilns, 554.
colours produced by, 118.
effect of, on colour, 116, 117.
minerals in clay, 422.
oxide in crystalline glazes, 398.
melting-point of, 605.
spinel, 400.
Chrysoberyl, 356.
Chrysotile, structure of, 25.
Chwarele ganister, texture of, 40.
Cimolite, 345.
Cinder tap, penetrative power of, 497.
Clamp bricks, 546.
Clark, F. W., 333, 347.
H. H., 293.
Clarke, 309.
Claus-Chance process, 238.
Clausmann, 504.
Clay and salt, effect of heat on, 352.
beds, effect of percolating water on, 506.
bricks, structure of, 17.
decomposition of, an irreversible reaction, 451.
definition of, 35, 344.
dehydration of, effect of, on specific heat, 595.
determination of felspar and quartz in, 40.
-felspar-flint mixtures, fusion of, 486.
formulæ, 346, 347, 348.
in aluminous minerals, 427.
ironstone, chalybite in, 420.
concretionary, 25.
oil from, 370.
pastes, best consistency of, 267.
drying, 295.
physical changes in, 257.
strength of, 170.
possible origins of, 354.
purpose of, in porcelain, 377.
-sand mixtures, dry, strength of, 171, 172.
separating colloidal matter from, 263.
separation of quartz and felspar from, 409.
of sand and silt from, 343.
-silica bricks, structure of, 18.

Clay *continued*—
slips, effect of salts on electrical resistivity of, 620.
electrical conductivity of, 619.
properties of, 619.
resistivity of, 620.
nature of, 10.
soluble in felspar, 483.
substance, 343.
suspensions, protection of, 249.
swelling of, in water, 237.
synthesis of, 352.
use of, in glazes, 386.
variable behaviour of water in, 338.
wares, apparent density of, 214.
thermal conductivity of, 587.
true specific gravity of, 214.
-with-flints, 424.
Clays, absorption of water by, 76, 254, 337.
adsorption by, 238.
of dyes by, 240.
of gases by, 239.
of grease by, 239.
of liquids by, 239.
of oil by, 239.
of salts by, 240.
of solids by, 239.
from solution by, 240.
of soluble substances by, 240.
adsorptive power of, 236.
alkalies in, 364.
apparent density of, 212.
as bond for carbides, 405.
as catalysts, 443.
as emulsoids, 237.
baked, structure of, 20.
ball, colour of, 107, 108 ; see also Ball clays.
binding power of, 281.
bleaching, 506.
Brinell hardness of, 126.
buff burning, 114.
burned, colour of, 108.
iron compounds in, 420.
specific gravity of, 213.
texture of, 36.
true specific gravity of, 214.
calcining, 544.
purpose of, 26.
calcium compounds in, 367.
calcareous matter in, 370.
chemical components of, 361.
constitution of, 340, 343.
chromite in, 430.
coefficient of expansion of, 571.
colloidal, 11.
gel in, 265.
matter in, 13.
measuring, 240, 251.
Clays *continued*—
colloidal properties of, 13, 228, 236.
water in, 370.
colour of, 95, 97.
colouration of, by carbonaceous matter, 106.
by iron oxide, 99.
colouring by reducing, 111.
materials in, 107.
common, 343.
crushing, 254.
strength of, 171.
decomposition of, by heat, 350, 351, 438, 490, 491, 545.
by lime, 479.
deflocculation of, 247.
disintegration of, 254, 256.
distribution of water in, 255.
dry, see Dry clays.
drying, 295.
effect of acid on, 275.
of added colloidal matter on, 271.
of alkalies on, 248, 275.
of alumina on refractoriness of, 364.
of bacteria on, 275.
on carbon monoxide, 238.
of colours on, 250.
of drying on strength of, 158.
of electrolytes on, 242.
of frost on, 254.
of fusion with sodium carbonate, 322.
of heat on, 337, 338, 348, 350, 351, 472, 508.
on porosity of, 69.
on specific gravity of, 212.
of iron compounds on colour of, 103.
strength of, 160.
of light on, 507.
of lime on, 368, 495.
of magnesia on shrinkage of, 568.
on vitrification range of, 568.
of, on coefficient of expansion of porcelain, 574.
of, on crazing, 387.
of silica in, on melting-point, 363.
on refractoriness, 364.
of soluble substances on, 242.
of steam on, 256.
of sulphuric acid on, 504.
of water of constitution on, 337.
of water on, 227, 228, 256.
of weathering on, 253.
electrical conductivity of, 609, 611.
properties of, 242.
evolution of water of constitution of, 350.
extensibility of, 276.
felspars in, 417.
ferruginous minerals in, 418–420.
fired, ideal structure of, 29.

Clays *continued*—
firing in oxidising atmosphere, 493.
flaky, 22.
flow of, under pressure, 273.
for bricks, 374.
for china-ware, 375.
for earthenware, 374.
for firebricks, 373.
for porcelain, 375.
free alumina in, 364.
Gault, colour produced by, 112.
grinding, 254.
hardness of, 123, 125.
heating curves of, 349.
hydrolysis of, 236, 263.
hygroscopic nature of, 254, 298.
impure, effect of heat on, 414.
impurities in, 362.
removing, 287.
iron compounds in, 366.
oxide in (state of), 359.
lime in, 367.
magnetic properties of, 621.
manganese compounds in, 368.
microscopical examination of, 406.
mineralogical composition of, 406, 411.
miscibility of, 250.
mobility of, 276.
moisture in, 370.
mottled, causes of colour of, 108.
nature of, 13.
not mixing, cause of, 239.
oiliness of, 276.
order of changes leading to fusion, 485.
organic colloid matter in, 284.
matter added to, 284.
over-drying, effect of, 336.
-heating, effect of, 336.
oxidation of, effects of, 256.
processes in, 507.
peptisation of, 247.
permeability of, 90.
phosphorous compounds in, 369.
plastic, porosity of, 75.
plasticity of, 257–274.
pure, 414.
purification of, 287.
purified, 412.
purpose of adding sand to, 374.
pyrites in, 369.
rate of wetting, 240.
raw, colours of, 107.
strength of, 148, 170.
red-burning, 109, 110.
causes of colour of, 109.
rehydration of, 337, 338, 349.
removal of iron from, by magnets, 621.
reversible changes in volume of, 571.
Ruabon, colour of, 109.
sampling, 360.
semi-permeability of, 250.
shrinkage of, 565.
silica as an impurity in, 363.
size of grains of silica in, 363.
slaking of, 227, 257.
specific heat of, 595.
stoneware, colour of, 108.
structure of, 19.
sulphur in, 369.
surface factor of, 56.
tensile strength of, 171.
titanic oxide in, 368.
true specific gravity of, 212.
ultramicroscopic examination of, 631.
vanadium compounds in, 369.
vitrification range of, 553.
vitrified, structure of, 20.
water of constitution in, 337.
of crystallisation in, 337.
of hydration in, 337.
required to develop plasticity of, 269.
weathering, 255.
white, 108.
yellow, colour in, cause of, 108.
Clews, F. H., 353.
Clinker bricks, Dutch, strength of, 173.
finishing temperature for, 555.
German, strength of, 175.
hardness of, 128.
strength of, 173, 174.
true specific gravity of, 215.
volume-weight of, 215.
Clinœnstatite, 481.
Coagulation by added colloid matter, 231.
causes of, 232.
Coagulative power of a salt, 231.
Coal ash, action of, on fireclay bricks, 496.
Coarse sand, definition of, 35.
Coating ware with engobe, 283.
Cobalt-blue glazes, 389, 395.
zeolites in, 389.
compounds, colour produced by, 118.
effect of, on colour, 116, 117.
oxide as colouring agent, 113, 118.
as decolorant, 113.
in crystalline glazes, 397, 398.
prepared, 395.
Cobaltite, space-lattice of, 324.
Cobb, J. W., 329, 339, 340, 352, 462, 466, 467, 468, 470, 495, 515, 516, 522, 571, 572, 579, 587, 588, 590, 592, 593.
Coefficient of expansion or contraction, 521.
of clays, 571.
of glazes, 578.
of porcelain, 577.

Coefficient of expansion *continued*—
of stoneware, 577.
of linear expansion, 580.
Cohesion, 140.
limit, 268.
of clay to iron, 239.
Cohn, 260.
Coke bricks, 404.
structure of, 17, 19.
texture of, 43.
colour of, 119.
in clay mixtures, 371.
ovens, formation of glaze in, 87.
porosity of bricks for, 78.
use of, for increasing porosity, 66.
Colliery refuse, bricks made from, 370.
Collins, J. H., 353.
Colloidal alumina, 251.
clays, 11.
gels, 7, 12.
changes in, during burning, 547.
contraction of, 235.
heating of, 13.
in clay, 265.
properties of, 235.
structure of, 12.
swelling of, 12.
iron, effect of, on sands, 252.
hydrate, effect of, 271.
magnesia, 253.
matter and binding power of clay, 281.
and plasticity, 262, 277.
behaviour of, on drying, 295.
coagulative action of, 231.
effect of adding, 271.
in clays, 13, 228, 251.
measuring, 240.
separation of, 263.
organic matter, 253.
particles, size of, 11.
phenomena, 228.
precipitates, nature of, 232.
properties of clays, 236.
reactions, 236.
importance of time on, 439.
silica, 252, 363, 424.
as a cementing material, 15.
effect of, 271.
inversion of, 13.
silicic acid, 252.
effect of drying on, 333.
sols, 11.
action of heat on, 235.
of salts on, 11.
adsorption by, 235.
Brownian movement in, 233.
diffusivity of, 234.
electric charge on, 228.
Colloidal sols *continued*—
electrical conductivity of, 230.
electro-osmosis in, 230.
kataphoresis in, 229.
osmotic pressure of, 233.
precipitation of, 230.
properties of, 228.
protection of, 232.
reversibility of, 235.
specific gravity of, 234.
volume of, 204.
stabilising, 233.
viscosity of, 234.
solution, 11.
state, defined, 11.
nature of materials in the, 228.
suspension, coarse, 11.
systems, 12.
water, 336, 358.
in clay, 370.
Colloids, active, 251.
atomic structure of, 322.
Brownian movement in, 11.
coagulable, measurement of, 277.
coagulated, dispersion of, 232.
crystalline, 11.
flocculation by, 243.
of, 11.
irreversible, 253.
molecular structure of, 322.
nature of, 1, 10.
precipitation of, 11.
by electrolytes, 231.
relative, 278.
Collyrite, 20, 345, 412.
structure of, 7.
Coloration by oxidation, 107.
Colour changes during burning, 547, 549.
in smoking, 544.
control of, 110.
due to algæ, 97.
irregular, cause of, 111.
measurement of, 123.
mottled, causes of, 111.
natural sources of, 96.
nature of, 94.
of ceramic materials and articles, see under their various names.
glaze, altering, 391.
streaks of, as decoration, 118.
variation of, 94
variegated, 118
Coloured engobes, 395.
glazes, 395.
oxides for, 397.
Colouring materials in clays, 107.
oxides in glazes, 389.
Colourmeter, use of, 123.

Colours, artificial, producing, 115.
blue, producing, 116.
brown, producing, 117.
buff, cause of, 99.
chocolate, producing, 118.
effect of alkalies on, 102.
firing temperature on, 100, 110, 118.
iron on, 98.
kiln atmosphere on, 118.
lime on, 102.
magnesia on, 102.
mode of burning on, 96.
on clays, 250.
finishing temperatures for, 555.
flowing of, 118.
green, producing, 116.
grey, producing, 116.
iron, effect of temperature of firing on, 100.
olive-green, producing, 116.
organic, in clays, 106.
produced by carbonaceous matter, 106.
by chromium compounds, 116, 117, 118.
by cobalt compounds, 113, 114, 116, 117, 118.
by copper compounds, 118.
by impurities, 96.
by iron chromate, 117.
compounds, 97, 105, 118.
destruction of, 101, 102.
effect of acid on, 98.
by iron silicates, 116, 117.
by manganese compounds, 116, 117, 118.
by nickel compounds, 118.
oxide, 116, 117.
by oxidation, 108.
by titanium compounds, 118.
by zinc oxide, 116, 117.
purple, cause of, 111.
red, causes of, 100.
effect of alumina on, 101.
minerals on, 101.
producing, 117.
temperature required to produce, 110.
use of engobes for, 96.
violet, producing, 116.
volatilisation of, 118.
yellow, in clays, cause of, 108.
producing, 117.
Comber, N. M., 244, 245, 278.
Combination, chemical, laws of, 302.
direct, 435.
heat of, 528, 529.
Combined water in alumina, 340.
Common bricks, see Building bricks.
Compensation, position of, 628.
test, 628.
Component, definition of, 453.
Composition and colour, 113.
electrical properties, 609.
fusing point of glazes, 384.
refractoriness, 381.
utility of clays, 371.
changes in, due to heat, 528.
effect of, on strength, 154.
on translucency, 632.
from molecular formula, 311.
of clays, 361.
of engobes, 382.
of glazes, 382.
adjustment of, 389.
of porcelains, 378.
of Seger cones, 379.
of silica bricks, 398.
-temperature diagrams, 465.
Compounds, 299.
atomic, 302.
chain, 308.
chemical, 299.
decomposed by electricity, 444.
formation of, 462.
molecular, 302.
ring, 308.
saturated, defined, 305.
unsaturated, defined, 305.
Compressibility and plasticity, 280.
Compressive strength, determination of, 195.
Concretionary structures, 25.
Conductivity, contact, 518.
electrical, 230, 444, 608, 609.
changes in, during burning, 548, 549.
determination of, 620.
effect of porosity on, 74.
of clay slips, 611, 619.
of silica bricks, 616.
of water, 619.
of heat, 514.
thermal, 514.
changes in, during burning, 548, 549.
effect of burning on, 590.
of heat on, 584.
in magnesia bricks, 591.
in silica bricks, 591.
of permeability on, 89.
of porosity on, 72, 74.
of temperature on, 587, 588.
of ceramic materials, see under their various names.
of powders, 592.
Conductors, bad, 609.
good, 609.
moderate, 609.
Cones, Seger, 540.
composition of, 379.
temperatures corresponding to, 379.

Consistency, 268.
of clay paste, 267.
of pastes, 278.
Constitution, chemical, of burned clay, 348.
of calcined clay, 348.
of ceramic materials, 299.
of clays, 340, 343.
of iron oxides and hydroxides, 357.
of lime, 357.
of magnesia, 355.
of silica, 326.
of silicates, 332.
of silicic acid, 332.
of silicon carbides and oxycarbides, 357.
of spinels, 356.
of sundry refractory materials, 358.
of water, 337.
Contact, area of, effect of, 446.
conductivity, 518.
of particles, effect of, on chemical action, 445.
resistance, 518.
Contraction, 520.
effect of, on melting-point, 526.
harmful, in retorts, 566.
of colloidal gels, 235.
Contraction on drying, 295.
Convection, 519.
Cook, 260.
Cooling, 559.
changes in, 559.
curves, 489.
v. heating curves, 466.
effect of, on allotropic forms, 560.
on composition of products, 489.
on strength, 560.
of kilns or ovens, 162.
effect of, on strength, 162.
rapid, 488.
effect of, 563.
on spalling, 584.
rate of, 162.
effect of, on crystallisation, 488.
on specific gravity, 211.
repeated, effect of, 563.
slow, 488.
Copper alloys, melting-points of, 541.
-blue glazes, zeolites in, 389.
compounds, colours produced by, 118.
discoloration produced by, 121.
glazes, 389.
-iron sulphides, 420.
melting-point of, 541.
metallic, in aventurine glazes, 398.
oxide as colouring agent, 118.
effect of, on silica glass, 498.
on zirconia bricks, 500.
in crystalline glazes, 397, 398.
in glazes, 395.
Copper oxide *continued*—
penetrative power of, 497.
spinel, 400.
sulphide, effect of weather on, 507.
thermal conductivity of, 587.
Coprolites, 367, 421, 422.
Cordierite, 418, 479.
birefringence of, 626.
electrical conductivity of, 609.
in clay, 421.
refractive index of, 623.
Cores, black, cause of, 105.
in clay, 423.
Cork, use of, to increase porosity, 66.
Cornish stone as bond in silica bricks, 399.
effect of, on porosity, 67.
erroneous replacement by, 314.
in glaze, 387.
Cornu, 339, 474.
Cornwall, china clay in, 414.
Corrosion, 494.
effect of graphite on, 371.
of porosity on, 73.
of texture on, 38.
measurement of, 500, 501.
of refractory materials, 481.
rate of, 446.
Corrosive substances, 494.
Corundum, 339, 421, 426, 480.
articles, texture of, 43.
artificial, 426.
birefringence of, 626.
bricks, hot, strength of, 165.
structure of, 17.
crystalline form of, 4.
structure of, 2, 14.
electrical conductivity of, 609.
hardness of, 126.
melting-point of, 605.
range of, 606.
pleochroism of, 630.
refractive index of, 623.
with sillimanite, 480.
with soda, 480.
Cracking bricks by lime, 374.
due to large grains, 16.
effect of grading on, 32.
Cracks, 163.
caused by cooling, 559.
in glaze, preventing, 390.
Crawford, J. L., 212.
Crazing, 384, 385, 386, 387, 389, 390, 392.
and expansion, 578.
caused by cooling, 559.
Cremiatschensky, 261.
Cristobalite, 328, 426, 475.
and sillimanite eutectic, 473.
determination of refractive index of, 625.

Cristobalite *continued*—
formation of, 329, 331, 443.
from tridymite, 331.
in furnace hearths, 17.
in silica bricks, 16.
latent heat of fusion of, 600.
melting-point of, 331, 603.
produced by cooling fused silica, 331.
rate of formation of, 330.
refractive index of, 623.
solubility of, in hydrofluoric acid, 504.
specific gravity of, 216.
heat of, 597.
Critical density, 485.
point in cooling fused material, 458.
pressure, 485.
temperature, 438, 485.
volume, 485.
Crocidolite, structure of, 25.
Cronshaw, 474.
Crook, T., 620, 621.
Cross, 315, 413.
Cross-breaking tests, 197.
Crucible clay, American, strength of, after drying, 159.
German, strength of, after drying, 159.
furnaces, porosity of bricks for, 78.
Crucibles, 404.
and their contents, 433.
burning, 557.
carbon, shrinkage of, 570.
casting, 284.
corrosion of, 495.
durability of, 582.
effect of repeated heating on, 563.
firing temperature of, 558.
interaction of, with contents, 491.
laminated structure in, 23.
permeability of, 90.
resistance of, to sudden changes in temperature, 582.
strength of, 183.
when hot, 165.
tensile strength of, 140.
texture of, 39.
zirconia, 79.
casting, 285.
" Crumbs " of clay, 261, 344.
Crushing strength, 144.
determination of, 195.
effect of exposure on, 167.
of frost on, 167.
of bricks, 173.
under load, heating schedule for, 197.
when hot, 164.
See also Strength.
Cryolite, effect of, on zirconia bricks, 500.
melting-point of, 606.
Cryptocrystalline magnesite, 427.
nodular, 25.
structure of, 8, 19.
texture of, 43.
true specific gravity of, 220.
structure, 15.
Crystalline forms, 2.
glazes, 397.
masses, nature of, 14.
materials, effect of heat on, 8.
matter in glaze, increasing, 390.
silica, occurrence of, 425.
solids, stability of, 488.
structure, coarse, 15.
disadvantages of, 14.
fine, 15.
value of, 14.
systems, 4.
Crystallisation, causing, 488.
degree of freedom necessary for, 487.
during cooling, 559.
effect of dust on, 489.
of number of centres of, on, 489.
of nuclei of, 489.
of rate of cooling on, 488.
of temperature on, 488.
of viscosity on, 488.
extent of, 633.
heat of, 528.
production of, 551.
water of, 371.
Crystallising agents, 397.
in matte glazes, 396.
Crystallites, 3.
nature of, 2.
Crystallographic axes, 4.
Crystallography, 4.
Crystalloid, nature of, 11.
Crystals, " bricks " of, 323.
cause of growth of, 324.
combination, 4.
formation of, 2, 563.
forms of, 4.
imperfect, in ceramic materials, 2.
imperfectly formed, 2.
in ceramic materials, 2.
in clay, 412.
incipient, 3.
isotropic, 627.
mixed, 324, 334, 335, 336, 489.
See also Mixed crystals.
nature of, 2.
optical identification of, 622.
perfectly formed, 2.
refractive index of, measuring, 624.
simple, 4.
structure of (space-lattice), 323.
systems of, 4.

Crystals *continued*—
zoned, 459.
Crystolon, 357, 404.
coefficient of expansion of, 581.
effect of alkalies and alkaline carbonates on, 504.
of hydrofluoric acid on, 504.
of metallic oxides on, 504.
Cube-lattice, 323.
Cubic expansion, 521.
Cunningham, E., 54.
Cupolas, resistance to abrasion, 125.
Cuprite, space-lattice of, 324.
Curie, 326.
Cushman, A. S., 271.
Cutter bricks, strength of, 173.
Cyanite, 342, 413, 480.
birefringence of, 626.
crystalline form of, 4.
electrical conductivity of, 609.
formation of clay from, 354.
hardness of, 126.
magnetic properties of, 621.
pleochroism of, 630.
refractive index of, 623.
thermal curve of, 352.

Damour, 385.
Dana, 216, 605.
Daubrée, 260.
Dauphin, 65.
Davidson, Charles, & Co., Ltd., 18.
Davies, H. E., 290.
Day, 331, 467, 525, 606, 607.
Dead-burned magnesia, 428.
composition of, 401.
Deccan, laterite in, 19.
Decolorising effect of alumina, 102.
of fluxes, 102.
of lime, 102.
of magnesia, 102.
Decomposition, 490.
double, 436.
stage in burning of ceramic materials, 545.
Decorating ware, 283.
by colours, 96.
Decoration, over-glaze, 96.
under-glaze, 96.
Deflocculants for clay, 285, 286.
Deflocculation, 246.
Deformability and plasticity, 277.
explained, 139, 144.
tests, 199.
Deformation of fireclay bricks at high temperatures, 179.
Degree (unit of temperature), 533.
Dehydration of clays, 237.
Density, 203.
and dielectric strength, 610.
apparent, 203, 205.
effect of mode of preparation and of manufacture on, 206.
of moisture on, 206.
of porosity on, 72, 205.
of temperature on, 205.
of texture on, 205.
factors influencing, 205.
See also Apparent density.
changes in, during burning, 548.
critical, 485.
See also Apparent density.
vapour, and molecular weight, 304.
Dental porcelain, 376, 378.
Derbyshire, pocket clays of, 506.
Des Cloizeaux, 412.
Desvignes, E., 131, 136.
Determination of electrical conductivity, 620.
resistivity, 620.
hardness, 134.
magnetic properties, 621.
melting-point, 526.
puncture voltage, 620.
refractoriness, 526.
softening-point, 526.
texture, 44–59.
Deveraux, 337.
Deville, 578.
furnace, 527.
Devitrification, 488, 563.
avoiding, 336, 389.
due to overheating, 562.
Devon, ball clay in, 414.
china clay in, 414.
Dextrin as a bond, 153.
Dextro-rotation, 629.
Diabase, specific heat of, 597.
Diallage, 415.
birefringence of, 626.
Dialysis, 251.
Diamond, electrical conductivity of, 609.
lustre of, 95.
refractive index of, 623.
Diaspore, 339, 402, 427.
bricks, resistant to slags, 499.
constitutional formula of, 340.
in clay, 421.
shrinkage of, 570.
Diatomaceous earth, 7.
Diatoms, 7.
Dichroic minerals, 630.
Dick, A. B., 625.
Diddier insulating bricks, apparent density of, 219.
specific gravity of, 219.
Didymia, source of, 21.

Dielectric strength, 608, 610.
effect of heat on, 614.
of lime on, 612.
of porosity on, 74.
of porcelain, 613.
decrease of, when heated, 615.
of silica glass, 617.
Dietrich, 614.
Diffusion, coefficient of, 517.
columns, use of, 408.
Diffusivity, 234, 517.
effect of heat on, in magnesia bricks, 591.
in silica bricks, 591.
of temperature on, 587.
of fireclay bricks, 587.
Dimetasilicate, 332.
Dimetasilicic acid, 333.
Dimorphous crystals, 5.
Dinas brick, specific gravity of, 596.
specific heat of, 596.
thermal conductivity of, 588.
rock, heat treatment of, 218.
sand, 20.
Diopside, 415, 474.
birefringence of, 626.
latent heat of fusion of, 601.
melting-point of, 601, 606.
refractive index of, 623.
specific heat of, 597.
Diorthosilicic acid, 333.
Direct combination, 435.
Discoloration, blue, cause of, 121.
brown, cause of, 121.
by kiln atmosphere, 121.
pyrites, 121.
soot, 121.
causes of, 121.
effect of porosity on, 74.
green, cause of, 121.
of china, cause of, 121.
of porcelain, cause of, 121.
pink, cause of, 121.
red, cause of, 121.
yellow, 122.
Disintegration by weathering, 506.
of clays, 254, 256.
Disperse phase, 11.
Dispersion medium, 11.
Displacement, chemical, 436.
Disposing affinity, 442.
Dissociation, 436, 490.
heat of, 531, 599.
pressure of calcium carbonate, 448.
Distortion, 560.
and rapid heating, 440.
cause of, 377, 550.
preventing, 285.
Ditte, 220, 356.
Dittler, 607.
Doelter, 461, 487, 488.
Dolomite, 402, 428.
action of hydrochloric acid on, 503.
water on, 503.
as a cementing material, 15.
birefringence of, 626.
bricks, 402.
strength of, 190.
texture of, 43.
true specific gravity of, 221.
calcining, purposes of, 26.
colour of, 120.
crystalline form of, 4.
decomposition of, 490.
electrical conductivity of, 609.
formation of, 506.
hardness of, 126.
in clay, 421.
in magnesite, 427.
isomorphism in, 5.
refractive index of, 623.
replacement of, by hæmatite, 5.
sands, 20.
sandstone, 25.
space-lattice of, 324.
specific gravity of, 221.
structure of, 14.
Domestic pottery, hardness of, 124.
Dorfner, 364, 368, 376.
Dorset, ball clay in, 414.
Double decomposition, 436, 490.
oxides, 480.
refraction, 625.
salts, 341.
Douda, H. W., 155.
Dougill, 515, 516, 587, 588, 590, 592, 593.
Drain-pipes, finishing temperature for, 555.
Dry clay, effect of moisture on strength of, 166.
hardness of, 126.
nature of, 297.
strength of, 148, 170, 171.
structure of, 20.
water absorbed by, 75.
pastes, nature of, 298.
substance in slip, determination of, 226.
Dryer white, 122.
Drying, 294.
changes in volume during, 297.
effect of, on permeability, 89.
on strength, 158.
heat in, 543.
size of grains on, 30, 296.
irregular, 297.
rate of, 296.
effect of porosity on, 75.
shrinkage on, 295.
Ductility, explained, 139, 192.

Dulong, 512.
Dummel, K., 281.
Dun, 613, 615.
Dunts, 162.
  caused by cooling, 559.
Dupuy, M. E. L., 183.
Durability and the slag test, 502.
  effect of texture on, 38.
  explained, 139.
  of crucibles, 582.
Durham fireclays, copper-iron sulphides in, 420.
    effect of weathering on, 255.
  ganister, texture of, 40.
Dust, effect of, on crystallisation, 489.
  resistance to, 125.
  sand, definition of, 35.
    size of grains in, 35.
    surface factor of, 56.
Dutch clinkers, strength of, 173.
Dyes, absorption of, by clay, 240.
Dyne, 509.

Earthenware, clays for, 374.
  effect of lime on, 368.
  finishing temperature of, 553, 555.
  glazes, 393.
  hardness of, 133.
  shrinkage of, 565.
  strength of, 177.
  texture of, 40.
Efflorescence, 75, 122.
Elastic modulus of glasses, 188.
  of glazes, 192.
Elasticity explained, 139, 143.
Electric current produced by pressure, 611.
  changes due to heat, 532.
  charge on colloidal particles, 228.
Electrical conductivity, 230, 444, 608, 609.
    determination of, 620.
    effect of porosity on, 74.
    of clay, 611.
    of clay slips, 619.
    of silica bricks, 616.
    of water, 619.
  insulating power of porcelain, 612.
    of stoneware, 612.
  insulator porcelain, coefficient of expansion of, 578.
  precipitation, 230.
  properties of ceramic materials, 608; see also under their various names.
    of clay slips, 619.
    of clays, 242, 608.
  pyrometers, 537.
  resistance, 608.
    pyrometers, 536.
  resistivity, 609.
Electrical resistivity *continued*—
    and temperature, 611.
    at high temperatures, 614.
    determination of, 620.
    effect of calcium sulphate on, 619.
      of electric current on, 611.
      of fluxes on, 613.
    of carborundum bricks, 619.
    of chromite bricks, 618.
    of fireclay bricks, 612.
    of magnesia bricks, 617.
    of silica bricks, 616.
    of zirconia bricks, 618.
Electricity, effect of, 444.
Electro-adsorption, 230.
Electro-osmosis, 230.
  and purification of clays, 289.
  of clay, 289.
Electrodes, apparent density of, 221.
  carbon, effect of, on magnesia bricks, 499.
    specific gravity of, 221.
Electrolytes, action of, on clay, 242.
  conductivity of, at different temperatures, 619.
  effect of adding, 231.
    on porosity, 68.
    on strength, 155.
    on viscosity of clay, 286.
      of colloids, 234.
  flocculating power of, 245.
  flocculation by, 243.
  precipitation by, 231.
  used for casting, 285.
Electronic layers, 305.
Electrons, 301.
Electrostatic separation, 409.
Elements defined, 299.
Ellam, H., 112.
Elutriation, 50.
Elutriators, 51–53.
Emery, 65, 132, 135, 157, 186, 189, 192, 280, 330, 496, 497, 498, 595, 596.
Emley, W. E., 280, 293.
Emulsion, colloidal, 12.
Emulsoid, 12.
Enamel kilns, finishing temperatures for, 555.
Enamels, 383.
Endell, K., 16, 179, 216, 217, 218, 568, 603.
Endomorphs, 3.
Endosmose, 230.
Endothermal changes, 350, 520.
Enfield bricks, strength of, 173.
Engelhorn, F., 400, 403.
Engineering bricks, finishing temperature of, 553.
  strength of, 173.
  vitrification of, 551.
English Ceramic Society, 522.

Engobes, adjustment of composition of, 389, 390.
application of, 283.
coloured, 96, 395.
composition of, 382.
effect of altering, 385.
fusibility of, adjusting, 390.
influence of constituents on, 385.
shrinkage of, adjusting, 390.
slips for, 283.
Enstatite, 415, 459.
birefringence of, 626.
latent heat of fusion of, 601.
melting-point of, 601, 606.
refractive index of, 623.
Enzymes, effect of, on plasticity, 275.
Epidote, 418.
action of hydrochloric acid on, 503.
as a cementing material, 15.
birefringence of, 626.
electrical conductivity of, 609.
formation of clay from, 354.
magnetic properties of, 621.
melting-point of, 606.
pleochroism of, 630.
refractive index of, 623.
Equations, chemical, 316.
Equilibrium dependent upon temperature, 438.
diagram, 454.
incomplete, 484.
production of, 434.
proportions necessary to produce, 451.
result of disturbing, 439.
stable, 434.
tendency to, 439.
thermal, 509.
Equivalent proportions, law of, 303.
Erg, 509.
Erosion, effect of porosity on, 73.
Erratic boulders, 18.
for silica bricks, 17.
Erubescite, 420.
effect of weather on, 507.
Eskola, P., 469, 476.
Estuarine beds, refractory sands in, 20.
Etching, use of, 407.
Eutectic, 459.
composition of, 461.
point, 459, 461.
Eutectics in clay-magnesia system, 481.
lime-silica system, 467.
potash-alumina-silica system, 480.
soda-alumina-silica system, 480.
Evans, 628.
Ewell bricks, 373.
Excessive heating, effects of, 560.
Exchange, mutual, 436.
Exothermal changes, 520.
reaction on adsorption of water by clay, 239.
Expansion, 520.
and insensitiveness, 580.
coefficient of, effect of chemical composition on, 573.
of felspar on, 573.
of flint on, 573.
of texture on, 576; see also Coefficient of expansion.
cubic, 521.
linear, 521.
of ball clay, coefficient of, 573.
of firebricks, coefficient of, 572.
effect of porosity on, 572.
of fused silica, coefficient of, 580.
of glazes, coefficient of, 578.
effect of oxides on, 579.
of porcelain, coefficient of, 577.
of tiles, coefficient, of, 573.
of vitrified claywares, 573.
permanent, 565.
residual, of silica bricks, 568, 569.
Exposure, effect of, on crushing strength of bricks, 167.
prolonged, effects of, 507.
to an electric current, effect of, on apparent density, 611.
Extensibility, 142.
of clay, 276.
testing, 142, 194.
Extension and plasticity, 279.
Extinction angle, 627.
Extrusion and plasticity, 279.
critical pressure of, 274.

Face-centred cube lattice, 323.
Facing bricks, control of colour of, 110.
hardness of, 128.
strength of, 174.
Factors, 510.
Fahrenheit, 509.
and Centigrade scales, 534.
Faience glazes, 393.
Farnley fireclay, coefficient of expansion of, 571.
Fayalite, 333, 416, 470, 478.
formation of, in silica bricks, 426, 497.
fused, 487.
in furnace hearths, 17.
melting-point of, 366, 606.
with zinc, 482.
Feathered glazes, 555.
Feathering caused by cooling, 559.
Federov, 335.
Feel of ceramic materials, 137.
Feldenheimer, W., 288.

Felspar, 302, 416.
and flint, eutectic of, 483.
and spinel, separation of spinel from, 461.
as a bond in silica bricks, 399.
as a cementing material, 15.
content and "Te" value, 610.
corrosive action of, 496.
crystalline form of, 4.
structure of, 2.
determination of, in clay, 410.
dissolves clay, 483.
effect of fineness of, on porosity of ware, 67.
of fusion of, on specific gravity, 211.
of, on coefficient of expansion, 573.
of, on crazing, 387.
of, on porosity, 66.
of, on refractoriness, 364.
electrical conductivity of, 609.
eutectics with iron oxide and lime, 482.
extinction angles of, 627.
formation of, 440.
fusing-point of, 462.
in clay, 360.
in glazes, 387.
in zirconia ore, 429.
isomorphism in, 334.
-kaolin mixtures, fusion curve of, 365.
particles, fusion of, 486.
phase diagram of, 463.
plagioclase, crystalline form of, 4; see also Plagioclase felspar.
replaceability in, 334.
replaced by hæmatite, 507.
by limonite, 507.
by zeolites, 507.
separation of, from clay, 409.
Felspathic glazes, 383.
mixtures, fusion of, 486.
Felted mass, production of, 551.
Fenner, 216, 328, 329, 331, 332.
Feret, M., 57.
Feret's triangular diagram, 58.
Ferguson, R. F., 166, 330, 495, 497, 498, 503, 570.
and Buddington, 482.
and Merwin, 474.
Ferments, effect of, on plasticity, 275.
Ferrates, 332, 503.
formation of, 471.
Ferric compounds, discoloration caused by, 121, 122.
in raw materials, 97.
hydroxide in raw materials, 97.
sol, effect of, on sand, 252.
oxide, 303, 357.
as base or acid, 322.
effect of, on porosity, 68.
heat of formation of, 531
Ferric oxide *continued*—
in analyses, 359.
in clay, 366.
in raw materials, 97.
melting-point of, 606.
sulphide a cause of colour, 97, 103.
Ferriferous amphiboles and pyroxenes, electrical conductivity of, 609.
cassiterite, electrical conductivity of, 609.
Ferro-alumino-silicates, effect of, on clay, 367.
-carbonyl compounds, discoloration caused by, 121.
-silicates, effect of, on clay, 367.
Ferrous carbonate a cause of colour, 97, 103.
in clay, 366.
blue colour produced by, 97.
compounds, colours produced by, 97.
discoloration caused by, 121.
effect of distribution of particles on colour of, 105.
of heat on, 492.
of size of particles on colour of, 105.
green colour produced by, 97.
in clays, 103.
in raw materials, 97.
metasilicate, melting-point of, 606.
oxide, 303, 357, 419.
colour produced by, 103.
heat of formation of, 531.
in clay, 366.
in raw materials, 97.
melting-point of, 606.
oxidation of, 492.
production of, in burning, 104.
reaction of, with silica, 470.
phosphate a cause of colour, 97, 112, 121.
sulphate, 419, 420.
scum caused by, 97.
water in, 423.
Ferruginous cement in rocks, 15.
minerals in clays, 420.
Féry optical pyrometer, 538.
radiation pyrometer, 539.
Fibrous structures, 25.
Fibrox, 404.
true specific gravity of, 221.
Fiebelhorn, 354.
Filaments in crystals, 3.
Filters, permeability of, 89.
to be highly porous, 77.
Findlay, 453.
Findlings quartzite, 17.
structure of, 18.
Fine sand, definition of, 35.
Fineness, effect of, on shrinkage, 565.
Finishing stage of firing, 544, 549.
temperatures of ceramic materials, 553.

Firebricks, resistance of, to frost, 73.
texture of, 38.
Fireclay and magnesia bricks, interaction of, 498.
and salt, effect of heat on, 352.
articles, effect of sulphur on, 68.
attack of, by lime compounds, 494.
Fireclay bricks and spalling, 584.
apparent density of, 214.
as catalyst, 443.
blotches of slag in, 115.
burning, 556.
catalytic action of, 443.
changes of strength in, 149.
contraction of, 566.
corrosive action of flue-dust on, 496.
of iron compounds on, 495.
of slag on, 495.
of steam on, 495.
deformation of, at high temperatures, 179.
diffusivity of, 587, 588.
effect of exposure on, 167.
of fluxes on, 149.
of lime on, 149.
of Portland cement on, 495.
of repeated heating on, 163.
of weathering on, 167.
of whiting on, 495.
expansion of, coefficient of, 572.
firing, 556.
temperature of, 558.
hardness of, 128, 130.
hot, resistance of, to abrasion, 131.
strength of, 165.
of under load, 179, 180.
interaction of, with other bricks, 491.
melting range of, 605.
minerals in, 415.
permeability of, 90.
porosity of, 77, 80.
refractoriness of, 602.
relation of fusibility and composition, 149.
resistance of, to abrasion, 130.
softening of, at high temperatures, 165.
specific gravity of, 588.
heat of, 588, 595, 596, 597.
strength of, 178.
susceptibility of, to sudden changes of temperature, 582.
thermal conductivity of, 585, 587, 588, 593.
effect of burning temperature on, 585.
resistivity of, 594.
transverse strength of, at high temperatures, 181.
Fireclay cement, refractoriness of, 602.
mortar, refractoriness of, 602.
tiles, transverse strength of, 182.
Fireclays, 343, 414.
bauxitic, 421.
burned, colour of, 114.
casting, 284.
chalybite in, 420.
colours of, 108.
composition of, 373.
copper-iron sulphides in, 420.
effect of heat on apparent specific gravity of, 208.
on porosity of, 68, 70.
of rate of heating on, 526.
felspars in, 417.
iron sulphide in, 419.
magnetic properties of, 621.
Northumbrian, barytes in, 15.
plastic, apparent density of, 212.
dry, strength of, 171, 172.
refractoriness of, 602.
size of grains in, 34.
specific gravity of, 213.
vitrification range of, 553.
water required to develop plasticity of, 269.
Fired clay, minerals in, 415; see also Burned clay.
Fireproof floors, porosity of, 77.
Firesand, 431.
colour of, 119.
Fire-shrinkage, 565.
Firestones, structure of, 19.
thermal resistivity of, 594.
Firing clays, oxidising atmosphere in, 493.
duration of, 162.
effect of carbonaceous matter on, 370.
of duration of, on strength, 162.
of heat in, 544.
of, on colour, 105, 110.
of rate of, 161.
manner and duration of, 632.
temperature and crushing strength, 161.
effect of, on crushing strength of clay, 161.
on modulus of rupture of silica bricks, 162.
See also Burning.
Firth, E. M., 70, 71, 206, 207, 210, 213.
Fischer, M. H., 286.
Fissile structure, 22.
Fissility of clays, 137.
Five Quarter fireclay seam, effect of weathering on, 255.
Flaky clays, 22.
effect of, 61.
particles, 27.
structure, 22.
Flaming, 118.
Flashing, 106, 114, 118.
Flat particles, 27.

Fletton bricks, strength of, 173.
Flexibility explained, 139, 143.
Flint, 424.
  bricks, specific gravity of, 219.
  calcining, purpose of, 26.
  clays, apparent density of, 212.
    water required to develop plasticity of, 269.
  coefficient of expansion of, 579.
  colloidal nature of, 7.
  colour of, 119.
  effect of, on alkaline solutions, 505.
    on coefficient of expansion of porcelain, 573, 575.
    repeated heating on, 218.
  formation of, 506.
  nodular, 25.
  recognition of, in bricks, etc., 415.
  soluble in felspar, 483.
  specific gravity changes in, 217.
  specific gravity of, 216, 217.
  use of, in silica bricks, 40.
Flocculation, effect of, on plasticity, 246.
  of clay, 243.
    after purification, 289.
  rate of, 243.
Floor tiles, coefficient of expansion of, 573.
  hardness of, 129.
  measuring strength of, 199.
  resistance of, to abrasion, 130.
    to traffic, 125.
Floors, fireproof, porosity of, 77.
  porous, 77.
Flour as a bond, 153.
Flow and plasticity, 273.
  mass, 274.
  surface, 274.
Flower pots to be highly porous, 77.
Flowing colours, 118.
Flue-dust, action of, on firebricks, 330, 496.
  effect of, on strength, 169.
Fluidity, 290.
  and pressure, 274.
  and water content, 273.
  limit of, 268.
  pressure of, 126.
Fluorides as catalysts, 443.
Fluorine as catalyst, 443.
  vapours, action of, on alumina, 443.
Fluorite, electrical conductivity of, 609.
  refractive index of, 623.
Fluorspar, effect of, on shrinkage of earthenware, 567.
    on terra-cotta, 148.
    on zirconia bricks, 500.
  electrical conductivity of, 609.
  replacement of, by hæmatite, 5.
  space-lattice of, 324.
Fluxes, 362.
  affinity of, for alumina, 315.
    for silica, 315.
  and corrosion, 494.
  basic, effect of, on silica bricks, 497.
  chemical activity of, 445.
  combination of, 436.
  decolorising effect of, 102.
  effect of, on clays and refractory materials, 149.
    on electrical resistivity, 613.
    on porosity, 66.
    on silica bricks, 498.
    on strength, 147, 160.
    on terra-cotta, 148.
    on translucency, 632.
  in brick clays, 374.
  in glazes, 386.
  maximum effect of, 478.
Fluxing, cause of, 481.
  power of glaze fluxes, 386.
  production of, by reduction, 493.
  oxides, use of RO for, 307.
Foliated structure, 23.
Fontainebleau sand, sand-calcites in, 15.
Foote, 560, 605.
Formula weight, 305.
Formulæ, 306.
  chemical, 306.
  molecular, 309.
    objections to, 314.
  rational, 308.
  structural, 308.
Forsterite, 333, 416, 468, 478, 481.
  melting-point of, 607.
Fossilised animal excreta, 367.
Foster, H. D., 65, 82, 196.
Fourier's Law, 517.
Foussereau, 614.
Fox, 385, 389, 395.
Foxwell, 332.
Frankenheim, 323.
Free silica, occurrence of, 424.
Freedom, degree of, definition of, 453.
Freezing, effect of, 168.
  tests, 201.
Freundlich, 231, 236, 246.
Friability, 138, 142.
Frit, defined, 116.
  kilns, porosity of bricks for, 78.
Fritted glazes, 385.
Fritting, 387.
  glaze materials, precautions in, 388.
Frost, effect of, on clay, 254.
  on crushing strength, 167.
  on firebricks, etc., 73.
  on glazed ware, 73.
  on steamed bricks, 74.
  on vitrified articles, 73.

"Fuel" for gas fires, 25.
Full-fire stage in burning ceramic ware, 548.
Fuller, 286.
Fuller's earth, 412.
Fulton, 270, 478.
Furnace gases, resistance to, 125.
hearths, cristobalite in, 17.
fayalite in, 17.
shape of grains in, 29.
texture of, 42.
tridymite in, 17.
linings, 433.
interaction of, with contents, 491.
sand for, 21, 42.
Furnaces, porosity of bricks for, 78.
siliceous hearths in, 17.
Fused alumina, 403.
changes in volume of, 570.
effect of, on electrical resistivity, 612.
bauxite, coefficient of expansion of, 581.
magnesia, hardness of, 132.
masses, constitution of, 486.
material, cooling of, 468.
effect of temperature on amount of, 485.
solvent action of, 442.
matter, effect of, on shrinkage, 567.
mixtures, changes in, on cooling, 457.
quartz, 400, 484.
ribbon-like crystallisation of, 327.
specific gravity of, 220.
thermal conductivity of, 592.
See also Fused silica.
silica, 400.
coefficient of expansion of, 580.
effect of repeatedly heating, 563.
electrical insulating properties of, 616.
glass, formation of, 331.
hardness of, 132.
increasing strength of, 150.
melting-point of, 603.
permeability of, 89.
thermal conductivity of, 591.
Fusibility explained, 139.
of engobes, adjusting, 390.
of glazes, increasing, 390.
order of, 485.
Fusible metals and salts as pyroscopes, 541.
Fusing-point, 484.
temperature of refractory materials and articles, 558.
Fusion, 484.
curve of felspar-kaolin mixtures, 365.
of mica-kaolin mixtures, 365.
curves, 463.
effect of duration of heat on, 485.
on alumino-silicates, 322.
Fusion *continued*—
effect of duration of heat on silicates, 336.
on specific gravity, 211.
heat, 598.
first signs of, 527.
latent heat of, 600.
order of changes leading to, 485.
partial, 485.
point, 525.
effect of bases on, 387.
of glazes, lowered by boric oxide, 389.
range, 486, 561.
rate of, 486.
superficial, 423.

Gadolinite, 488.
Gahnite, 356, 482.
Galena, melting-point of, 607.
Ganister, 17, 425, 472.
bastard, Scottish, texture of, 40.
bricks, 17.
after-expansion of, 569.
American, 186.
Chwarele, texture of, 40.
coefficient of expansion of, 579, 580.
colour of, 119.
composition of, 400.
Durham, texture of, 40.
North Wales, texture of, 40.
Yorkshire, texture of, 40.
Sheffield, texture of, 40.
South Yorkshire, silification of, 19.
texture of, 40.
Garnet, electrical conductivity of, 609.
formation of, 440.
of clay from, 354.
magnetic properties of, 621.
refractive index of, 623.
Gary, M., 179.
Gas thermometers, 536.
Gaseous bubbles in crystals, 3.
Gases in furnaces, resistance to, 125.
Gasification, latent heat of, 524.
Gault bricks, strength of, 173.
clays, colour of, after burning, 112.
coprolites in, 422.
Gautier, 504.
Gebauer, 166.
Gehlenite, 479, 482.
melting range of, 607.
replacement in, 335.
Gelatin, effect of, on plasticity, 275.
Gelatinous silica, solubility of, in hydrofluoric acid, 504.
Geller, P. F., 182, 241, 337.
Gels, colloidal, 12.
water in, 12; see also Colloidal gels.

German Admiralty, 602, 603.
silica bricks, specific gravity of, 219.
Geyserite, 253, 424.
effect of repeated heating on, 218.
Gibbs, W., 453.
Gibbsite, 339, 427.
constitutional formula of, 340.
shrinkage of, 570.
Gilchrist, 613, 632.
Gilles, S. W., 214, 590.
Gillet, 493.
Ginsberg, 607.
Gioberite, 427.
Glamorganshire, Dinas sand in, 20.
Glasgow fireclay, coefficient of expansion of, 571.
Glass a solid solution, 336.
annealing, 559.
coefficient of expansion of, 576.
colours, finishing temperature of, 555.
cooling, 559.
corrosive action of, 496.
crystallisation of, 355.
devitrification of, 355.
electrical resistivity of, 617.
formation of, during vitrification, 552.
hardness of, 132.
modulus of elasticity of, 188.
pot mixtures, coefficient of expansion of, 571.
pots, 183.
burning, 557.
casting, 284.
firing temperature of, 558.
ideal structure of, 17.
porosity of, 78.
refractoriness of, 604.
resistance of, to sudden changes of temperature, 582.
texture of, 39.
thermal conductivity of, 593.
resistivity of, 594.
production of, 485.
quartz, 6; see also Silica glass.
specific heat of, 597.
tank blocks, porosity of, 78.
texture of, 39.
Glasses, 487.
chemical constitution of, 354.
tendency of, to crystallise, 489.
Glasson, J. L., 325.
Glassy bonds, 154.
cements, 16.
lustre, 95.
material, action of, in burning, 558.
matrix in bricks, 16.
in rocks, 16.
matter and translucency, 633.
in ceramic materials, 485.
Glassy bonds *continued*—
state, see Vitreous state.
substances, 6.
use of, in ceramic materials, 6.
Glauconite, 416.
Glaucophane, 342, 415.
refractive index of, 623.
Glaze fluxes, power of, 386.
formation of, in coke ovens, 87.
slip, absorption of, by clay, 239.
Glazed bricks, finishing temperature for, 555.
ware, firing, 554.
permeability of, 90.
resistance of, to abrasion, 133.
Glazes, 383.
adjustment of composition of, 389.
alumina-silica ratio in, 386.
as solid solutions, 336.
aventurine, 398.
avoiding crystallisation in, 336.
boiling of, 561.
Bristol, 392.
chemical constitution of, 354.
clarifying, 385.
coefficient of expansion of, 578.
colour of, altering, 390, 391.
coloured, 395.
oxides for, 397.
colouring oxides in, 389.
composition and fusion-point of, 384.
crystalline, 355, 397.
matter in, increasing, 390.
crystallisation of, 355.
devitrification of, 355.
dulling of, 561, 562.
earthenware, 393.
effect of altering composition of, 385.
of oxides on coefficient of expansion of, 579.
elastic modulus of, 192.
excessive heating of, 562.
faience, 393.
feathered, 555.
for various kinds of ware, 391.
fritting, precautions in, 388.
fused in burning, 548.
fusibility of, increasing, 390.
fusion point of, lowered by boric oxide, 389.
hardness of, 133.
influence of constituents on, 385.
lead *v.* leadless, 388.
matte, 355, 396.
nature of, 6.
opalescent, 395.
pink, production of, 117, 395.
poisonous, 388.
porcelain, 393.
proportion soluble in acid, 388.

Glazes *continued*—
salt, 391.
sanitary ware, 392.
shrinkage of, altering, 390, 391.
slips for, 283.
soda in, effect of, 398.
soluble, salts in, 387.
stoneware, 392.
strength of, 192.
tendency of, to crystallise, 489.
tensile strength of, 140.
terra-cotta, 392.
typical, 391.
use of alumina in, 385.
of clay in, 386.
of fluxes in, 386.
of silica in, 385.
zeolites in, 389.
Glenboig clay, halloysite in, 412.
firebricks, resistance of, to sudden changes of temperature, 582.
Globulites, 3.
Glossiness, cause of, 622.
Glost-firing, 554.
ware, colour of, 112.
Glue as a bond, 153.
Glycerin, as bond for carbides, 405.
Goecke, 605.
Goerens, P., 214, 516, 590.
Gold alloys, melting-point of, 541.
melting-point of, 541.
metallic, in aventurine glazes, 398.
Goodwin, 605, 614.
Gosrow, 133.
Gothite, 419.
Gouy, 232.
Grading, 31.
effect of, on cracking, 32.
on permeability, 31.
on porosity, 31, 32.
on spalling, 32.
on strength, 152.
on texture, 31, 32.
on voids, 32.
silica bricks, 41.
Graham, Thomas, 10, 11,
Grain-size, effect of, on crushing strength, 151.
on inversion of silica, 330.
Grains, angular, 27.
rounded, 27.
shapes of, 27.
size of, 29.
Granger, A., 43.
Granite, components of, 454.
electrical conductivity of, 609.
Grant, 280.
Granular structure, 15.
types of, 16.
Graphic formulæ, 308.
Graphite, Alabama, 23.
bricks, permeability of, 90.
porosity of, 80.
structure of, 17.
thermal conductivity of, 592, 593.
effect of firing temperature on, 585.
Ceylon, 23.
colour of, 119.
crucibles, burning, 558.
effect of, on corrosion, 371.
for crucibles, 404.
hardness of, 126.
Madagascar, 23.
occurrence of, 430.
Pennsylvanian, 23.
slabs, texture of, 43.
specific gravity of, 221.
structure of, 7, 8, 23.
thermal conductivity of, 592.
resistivity of, 594.
use of, 430.
Grease adsorbed by clay, 239.
Greasy feel of ceramic materials, 137.
Grecian magnesite, colour of, 120.
Green, A. T., 515, 517, 587, 589, 590, 591.
Green, S. A., 57, 244, 247, 272.
colour in burned clays, 369.
produced by iron compounds, 97.
producing, 116.
discoloration, cause of, 121.
glaze, 395.
Greening & Son, N., 45.
Greensand beds, phosphatic nodules in, 422.
Greiger, C. F., 184.
Griffiths, 516.
Grey articles, producing, 116.
colours produced by iron compounds, 97.
scum, 123.
Grinding, alteration of structure by, 26.
effect of, on strength, 154.
mills, shape of grains produced by, 29.
Grog, 18.
bricks, apparent density of, 214.
refractoriness of, 603.
specific gravity, 214, 596.
heat, 596.
strength of, 178.
structure of, 18.
thermal conductivity of, 588, 590.
casting, 284.
constitution of, 348.
effect of size of, on strength, 151.
firing temperature of, 558.
size of, for retorts, 39.
texture of, 36, 37.
use of, for increasing porosity, 66.
Gross, 253.

Grossalmerode fireclay, specific gravity of, 213.
Grossular, melting range of, 607.
Groth, 309, 348.
Grout, F. F., 221, 262.
Growth of crystals, cause of, 324.
Grum Grzmailo, 329, 606.
Grünerite, 470.
Guest, 325.
Guldberg, 448.
Gum, effect of, on plasticity, 275.
Gurther, 606.
Guy, J. P., 249.
Gypsum, 367, 369, 421.
  as a cementing material, 15.
  decomposition of, by heat, 545.
  effect of weather on, 507.
  electrical conductivity of, 609.
  occurrence of, 428.
  plates, 628.
  refractive index of, 623.
  replacement of, by quartz, 5.

Hæmatite, 418.
  as a cementing material, 15.
  concretionary, 25.
  corrosive action of, 496.
  crystalline form of, 4.
  electrical conductivity of, 609.
  hardness of, 126.
  magnetic properties of, 621.
  red colour due to, 97,
  refractive index of, 623.
  replacement of, by quartz, 5.
  space-lattice of, 324.
Halifax fireclay, specific gravity of, 213.
Hall, A. D., 245.
Halle porcelain, 375.
Halloysite, 20, 345, 412.
  action of hydrochloric acid on, 503.
  drying, 337.
  refractive index of, 623.
  structure of, 7.
  thermal curve of, 352.
  water in, 423.
Hampshire, red-burning clays of, 109.
Hansen, J. E., 310.
Hard bricks, resistance of, to frost, 169.
  -burned ware, true specific gravity of, 215.
    volume-weight of, 215.
  -paste porcelain, 375.
  porcelain, apparent density of, 214.
  wares, hardness of, 127.
Hardness, Brinell's ball test for, 135.
  changes in, during burning, 547.
    in during smoking, 545.
  determination of, 124, 134.
Hardness *continued*—
  Mohs' scale of, 124.
  of ceramic materials and articles, see under their various names.
  Shore scleroscope for testing, 136.
Hardy, 245.
Harker, 461.
Harmotine, 342.
Hartmann, M. L., 130, 131, 132, 134, 181, 583, 584, 612, 616, 617, 618, 619.
Harvard, 80, 186, 492, 593.
Hatch, 507.
Hauerite, space-lattice of, 324.
Hauschofer, 348.
Haüy, 323.
Hauyne, formation of clay from, 354.
Heat, 508.
  absorption of, 519.
  and optical properties, 532.
  atomic, 512.
  calculations, 510.
  capacity, 510.
    of ceramic materials, 594.
  changes effected by, 519.
    in chemical composition, effected by, 528.
  conductivity, 514.
  decomposition of clay by, 438.
  dissociation of materials by, 436.
  effect of, in burning or firing ceramic materials, 544.
    in drying, 543.
    on alumino-silicates, 322.
    on amorphous materials, 8.
    on ceramic materials, 508, 543.
    on chemical reactions, 437.
    on china clay-felspar mixtures, 66.
      molecule, 347.
    on clay, 348, 350, 351.
    on colour, 100, 105.
    on crystalline materials, 8.
    on iron oxide, 357.
    on limestone, 440.
    on permeability, 88.
    on porosity, 66.
    on quartz, 330.
    on refractoriness, 601.
    on shape of grains, 407.
    on souring pottery mixtures, 275.
    on specific gravity, 211.
      of silica bricks, 217.
    heat, 594.
    on thermal conductivity, 584.
    on volume of a material, 563, 564.
    withdrawing, 559.
  electrical changes caused by, 532.
  evolution of, 528.
  evolved when clay is wetted, 239.
  general effects of, 519.

Heat *continued*—
latent, 523.
molal, 524.
of fusion, 523.
of vaporisation, 524.
loss of, through furnace walls, 518.
measurement, 509.
of combination, 528, 529.
of crystallisation, 528.
of dissociation, 531, 599.
of formation and mode of formation, 531.
of silicates, 599.
of various oxides, 531.
of neutralisation, 530.
of reaction, 530.
physical changes effected by, 528.
quantity of, 510.
rate of passage through ceramic materials, 584, 585.
recorders, 540.
relation of, to temperature, 508.
sensible, 520, 523.
transmission of, 514.
treatment and dielectric strength, 610.
Heath, A., 57, 66, 83, 85.
Heating curve of china clay, 349.
curves *v.* cooling curves, 466.
diagrams, 465.
duration of, effect of, on fusion, 485.
on specific gravity, 209.
effect of, on composition of products, 489.
excessive, 560.
phase conditions in, 466.
prolonged, effect of, 439, 550, 562.
on melting-point, 526.
on silica bricks, 497.
rapid, results of, 440, 563.
rate of, effect of, on melting-point, 526.
repeated, 163.
effect of, 563.
on specific gravity of siliceous materials, 218.
schedule for crushing test under load, 197.
substances, reasons for, 445.
too rapid, 371, 492.
Heats of reaction in ceramic processes, 599.
obscured, 531.
of solution, 529, 599.
of transition of silicates, 600.
Heavy liquids, use of, 408.
Hedvall, 468, 498.
Heinecke's porcelain, 378.
Helmholtz, 229.
Hempel, 605.
Henderson, 615.
Henning, F., 580, 581.
Hercynite, 471.
Hering, C., 593, 594.
Herman, 264, 606, 607.
Hermodorfer hard porcelain, strength of, 178.
Hertwig-Möhrenbach, 376.
Herzfield, 260.
Hess's law, 531.
Heyn, 518, 588, 590, 592, 596.
Hill, E. C., 148.
C. W., 123.
Hilpert, 606.
Hind, S. R., 284, 287.
Hirsch, 495.
Hodkin, F. W., 71, 206, 207, 213.
Hodsman, 515, 516, 522, 587, 588, 590, 592, 593.
Hohenbocke sand, heat treatment of, 218.
Holborn, 578, 581.
-Kurlbaum pyrometer, 538.
Holdcroft, 309, 337, 348, 350, 351, 595, 596, 598.
Holdcroft's thermoscopes, 540.
Holland, 19.
Hollow blocks, porosity of, 77.
bricks, strength of, 150.
refractory ware, strength of, 183.
Homogeneity, 59.
essential, 21.
Homogeneous mixtures, preparation of, 283.
structures, 21.
Honaman, R. K., 615.
Honda, 357.
Honey, effect of, in souring pottery mixtures, 275.
Hongen, O. A., 131, 150, 164, 401, 468, 583, 584.
Hope, H., 377, 567.
Hopkins, 384.
Hornblende, 415.
as a cementing material, 15.
birefringence of, 626.
crystalline form of, 4.
magnetic properties of, 621.
melting range of, 607.
pleochroism of, 630.
refractive index of, 623.
Horning, R. H., 586.
Hornung, 516.
Hostetter, J. C., 357.
Houldsworth, 329, 339, 340, 352, 571, 572, 579.
Hovestadt, 385.
Howarth, H. F., 260, 608, 613, 614.
Howat, W. L., 145, 171, 288.
Howe, R. M., 79, 156, 161, 166, 187, 189, 217, 495, 497, 498, 499, 502, 503, 568, 570.
Hromatko, J. S., 178, 198.
Hruda, T., 123, 369.
Hull, 424.
Humber silt, colour of bricks from, 110.
Humus, 232.
Hursh, R. H., 634.
Hutchings, 15.

Hyalite, 253.
Hyalophane, 417.
Hydrargillite, 339.
Hydrate defined, 319.
Hydrated silica, 363.
  effect of repeated heating on, 218.
Hydration, 507.
Hydraulic bonds, 154.
  properties of silicates, 503.
Hydrochloric acid, action of, on calcareous and ferruginous substances, 503.
  heat of solution of, 529.
Hydrofluoric acid, effect of, 504.
Hydrogel, 12.
Hydrogen sulphide, effect of clay on, 238.
Hydrolysis, 507.
  an endothermal reaction, 520.
  and mass action, 448.
  of clay, 236, 263.
  of silicates, 507.
Hydromagnesite, colour of, 120.
  hardness of, 126.
  structure of, 8.
  true specific gravity of, 220.
Hydromica, 412.
Hydrosol, 12.
Hydrous minerals, decomposition of by heat, 545.
  silicates, 336.
Hydroxide defined, 319.
Hydroxyl group, 319.
Hygroscopicity of clays, 237, 298.
Hypersthene, 415.
  birefringence of, 626.
  magnetic properties of, 621.
  pleochroism of, 630.
  refractive index, 623.
Hysteresis of silica gel, 252.

Ice, effect of, 254.
Iceland, geyserite in, 422.
Iddings, 315, 413, 486.
Identification of ceramic materials by optical properties, 622.
Idocrase, birefringence of, 626.
Ilmenite, 429.
  crystalline form of, 4.
  electrical conductivity of, 609.
  hardness of, 126.
  in clay, 421.
  magnetic properties of, 621.
Impact strength, determination of, 198.
  tests, 198.
Impermeability, 87.
  and finishing temperature, 558.
  of chemical ware, 90.
  of crucibles, 90.
Impermeability *continued*—
  of glazed ware, 90.
  of retorts, 90.
  of stoneware, 90.
Impermeable ware, 76.
Impurities and refractoriness, 362.
  carbonaceous, as colouring agents, 106.
  colour caused by, 96.
    -producing, 96.
  conversion of, 491.
  dissociated by heat, 436.
  effect of, on blue colour, 105.
    on melting-point, 485, 526.
    on specific gravity, 209.
  in aluminous minerals, 427.
  in carbides and carboxides, 431.
  in ceramic materials, 362.
    electrical conductivity of, 610.
  in chromite, 430.
  in clays, 362, 414–423.
    oxidation of, 492.
  in graphite, 430.
  in kieselguhr, 426.
  in magnesite, 427.
  in silica rocks, 426.
  in tripoli, 426.
  in zirconium minerals, 429.
  removal of, from clay, 287.
  volatilisation of, 491.
Incandescence, 519.
Incipient crystals, 3.
Inclusions in crystals, 3.
Incomplete equilibrium, 484.
  reactions, 449.
Indentation, resistance to, 124.
  tests, 135.
Indigo, adsorption of, by clay, 240.
Inductive capacity of silica glass, 617.
Indurated clays, 237, 370.
Ingersoll, L. R., 587.
Insensitiveness and expansion, 580.
Institute of Gas Engineers, 78, 186, 195, 196, 373, 400, 527, 557, 566, 568, 602, 603, 604.
  Mining and Metallurgy, 45.
I.M.M. standard sieves, 45, 46.
Insulating bricks, thermal conductivity of at various temperatures, 586.
  power, electrical, and temperature, 611.
    of porcelain, 612.
    of stoneware, 612.
    thermal, and porosity, 515.
      and texture, 515.
Insulators, electrical, 608.
    resistance of, at high temperatures, 616.
  " Te " value of, 615.
Interference, 630.
Interlocking grains, effect of shape on, 28.

Intimacy of association, 445.
Inulin, effect of, on plasticity, 275.
Ion, common, effect of, on eutectic composition, 461.
  defined, 306, 317.
Ionisation theory, 444.
Ionised solutions, 530.
Iridescence, 94.
Iron as a catalyst, 443.
  -bearing minerals, 418.
  carbide, effect of on colour of clay, 104.
  carbonate (ferrous) a cause of colour, 97.
    as a cementing material, 15.
  carbonyl, effect of, on colour of clay, 104.
  chromate, effect of, on colour, 117.
  compounds, colour of, effect of firing on, 100.
      produced by, 97, 118.
    corrosive, 495.
    decomposition of, by heat, 491, 546.
    destruction of colour due to, 101, 102.
    effect of carbonaceous matter on, 370.
      on colour, 98, 103.
  compounds, hydrolysis of, 507.
    in aluminous minerals, 421.
    in burned ware, 98.
    in clays, 366, 418.
    in fireclays, 373.
    in magnesite, 427, 428.
    in raw materials, 97.
    in silica bricks, 426.
    oxidation of, 491, 492.
    produced by burning, 100, 103, 104, 105.
    reduction of, 104.
    size and distribution of particles of, 105.
      See also Ferric compounds and Ferrous compounds.
  hydrates a cause of colour, 97.
  in fireclays, form of occurrence of, 103.
  -magnesium-mica system, 417.
  metallic, in aventurine glazes, 398.
  oxide-alumina system, 471.
    effect of, on strength, 160.
    -lime system, 471.
    -magnesia-silica system, 478.
      system, 474.
    magnetic, in raw materials, 97.
    -silica systems, 470.
  oxides, action of hydrochloric acid on, 503.
    as causes of colour, 97.
    as cementing materials, 15.
    concretionary, 25.
    constitution of, 357.
    effect of, on colour of magnesia, 120.
      of heat on, 357.
      on silica bricks, 497.
      on zirconia bricks, 500.
    eutectics with felspar, 482.
    in analyses, 359.
Iron oxides *continued*—
    in aventurine glazes, 398.
    in crystalline glazes, 397, 398.
    in magnesite, 401.
    in zirconia ore, 429.
    reduction of, in burning, 104.
    resistance of, to basic open-hearth slag, 498.
    state of, in clays, 359.
  penetrative power of, 497.
  phosphates, colour produced by, 97, 112.
  pyrites, electrical conductivity of, 609.
  removal of, by magnets, 621.
  salts, artificial colouration by, 99.
  silicates, effect of, on colour, 116, 117.
  spinel, 400.
  sulphide (ferric), a cause of colour, 97.
  sulphides, 419.
    action of, 495.
    as cementing materials, 15.
    effect of weather on, 507.
    on zirconia bricks, 500.
Irreversible colloids, 235, 253.
  reactions, 450.
  volume-changes, 520.
Isle of Rum, ultrabasic rocks in, 461.
Iso-electric point, 231.
Isomeric, 302.
Isomorphism, 5, 302, 334.
Isomorphous, 302.
  elements, 335.
  minerals, 5.
  mixture, 334, 341.
    formulæ of, 335.
  silicates, 334.
Isotopes, 299.
Isotropic crystals, 627.
  minerals, 406.
Ivory ball clay, 108.

Jachum, P., 281.
Jackson, W., 56, 57.
Jaeger, 469, 470.
Jameson, A. B., 354.
Japanese porcelain, 376.
  glazes for, 394.
Jaune de cuisson, 121.
Jelly, nature of, 12.
Jena glass, modulus of elasticity of, 188.
Johnson, 260, 265.
Joints of brickwork, thermal conductivity of, 593.
Joly, 598.
Jones, J. C., 69, 168.
Joule, 300, 509.

Kallauner, O., 123, 369.
Kanolt, C., 527, 604, 605.

Kaolin, 345.
adsorption of alkali by, 241.
birefringence of, 626.
burned, colour of, 109.
casting, 284.
clay-substance from, 344.
coefficient of expansion of, 571.
colour of, 107.
composition of, 372.
crushing strength of, 187.
dehydration of, 599.
dry plastic, strength of, 171, 172.
primary, strength of, 171, 172.
effect of Cornish stone on porosity of, 67.
of heat on porosity of, 71.
of magnesite on, 368.
of vanadium on, 369.
melting range of, 605.
organic matter in, 422.
size of grains in, 33.
specific gravity of, 210.
heat of, 595.
variable behaviour of water in, 338.
vitrification range of, 553.
water required to develop plasticity of, 269.
See also China clay.
Kaolinite, 412.
crystalline form of, 4.
effect of heat on, 350.
graphic formulæ for, 346.
hardness of, 126.
in china clay, 20.
refractive index of, 623.
water in, 423.
Kataphoresis, 229, 249.
Keane, L. A., 101.
Keele, J., 67.
Keeler, 386.
Keppeler, 339.
Kerl, B., 76.
Kerr, W. R., 156, 161, 217, 568.
Kieselguhr, apparent density of, 220.
bricks, strength of, 188.
structure of, 18.
thermal conductivity of, 591, 592.
resistivity of, 594.
carbonaceous matter in, 430.
colour of, 119.
green, 119.
permeability of, 90.
porosity of, 79, 80.
specific gravity of, 216.
structure of, 7.
thermal conductivity of, 585, 586, 593.
at various temperatures, 586.
resistivity of, 594.
use of, for increasing porosity, 66.
Kiln atmosphere, a cause of discoloration, 121.
effect of, on colour, 118.
contraction, 570.
gases, a cause of scum, 122.
gases, effect of, 493.
white, 122.
Kilns, atmosphere in, 162.
cooling, 162.
porosity of bricks for, 78.
resistance of, to abrasion, 125.
Kilwinning aluminous shale, specific gravity of, 213.
fireclay, specific gravity of, 213.
Kinney, 57.
Kinnison, 619.
Klein, A. A., 488.
Klinefelter, 613, 632.
Knett, 352.
Knollman, H. J., 151, 214, 215.
Knote, J. M., 212, 213, 350, 351, 595.
Kobler, F. E., 130, 132, 134, 181.
Koerner, 263, 397.
Kohl, H, 248.
Kohlmeyer, 606.
Kolk, 624.
Kolthoff, I. M., 230, 242.
Kopp, 514.
Kowalke, O. L., 150, 164, 401, 468.
Krehbiel, 397, 398.
Krehbiel's elutriator, 52.
Kyropoulos, 329.

Labradorite, 417.
birefringence of, 626.
effect of fusion on specific gravity of, 211.
fused, 487.
melting-point of, 607.
refractive index of, 623.
Laclede-Christy bond clay, 242.
Lacroix, 331.
Ladd, 280.
Laevo-rotation, 629.
Laird, J. S., 177, 337.
Lamb, 229.
Laminated structure, 22.
nature and cause of, 22.
Lamination, effect of size of grains on, 31.
in crucibles, 23.
in finished goods, 22.
in graphite, 23.
in raw materials, 22.
in retorts, cause of, 22.
in saggers, cause of, 23.
Lampen, 493, 605.
Lancashire red-burning clays, 109.
Landolt, 594.
Landrieu, P., 324.
Lange, O., 16.

Langenbeck, 281, 409.
Langmuir, 305, 324.
Lanthanum oxide, melting-point of, 605.
  source of, 21.
Laschtschenko, 598.
Latent heat, 523.
  of fusion, 523, 600.
  of gasification, 524.
  of vaporisation, 524.
Laterite, 427.
  colour of, 97.
  in clay, 421.
  nodular structure of, 25.
  structure of, 19.
Lattice-structure of compounds, 323.
Laumonite, 342.
Lauschke, G., 79.
Law of mass action, 446, 449.
Lawrence, 633.
Laws of chemical action, 432.
Lead Commission, results of, 388.
  compounds in glazes, 388.
    poisonous nature of, 388.
  glazes, 383.
    blackening of, 555.
    effect of alumina on, 385.
  oxide, effect of, on expansion of glazes, 579.
    on silica glass, 498.
  soluble in glazes, 388.
Leadless *v.* lead glazes, 388.
Lebedew, P., 607.
Le Chatelier, F., 144.
  H., 135, 144, 145, 186, 187, 189, 213, 225, 260, 329, 331, 356, 439, 538, 580.
Lechatelierite, 424.
Lees, 589.
Leicestershire red bricks, strength of, 173.
  red-burning clays of, 109.
  red marls, 109.
Leighton Buzzard sand, texture of, 42.
Lenzenite, 412.
Lepidolite, 342, 417.
  melting range of, 607.
  refractive index of, 623.
Leucite, 342, 480.
  action of hydrochloric acid on, 503.
  formation of, 440.
  formation of clay from, 354.
  latent heat of fusion of, 601.
  melting-point of, 601.
  melting range of, 607.
  refractive index of, 623.
Leucoxene, 429.
Lewis, W. H., 237.
L'Hermite, 250.
Lias clay bricks, thermal conductivity of, 590.
  true specific gravity of, 214.
Libman, 470.
Lickey quartzite, silicification of, 19.
Lienau, 427.
Liesbach, 488.
Liesgang, 24.
  rings, 24.
Light, absorption of, 622.
  bricks, carbonaceous matter in, 65.
  clay, porosity of, 80.
  effect of, on chemical reactions, 444.
  reflection of, 622.
  -weight silica bricks, thermal conductivity of, 590.
    effect of, on clays, 507.
Lime, allotrophic forms of, 357.
  -alumina-silica system, 478.
  -alumina system, 470.
  and alumina, interaction of, 470.
  and silica, interaction of, 434.
  as a bond, 154, 399, 405.
  -barium oxide-silica system, 474.
  bricks, strength of, 192.
    structure of, 17.
  burning, 490.
    effect of vapour-pressure on, 441.
  colour of, 120.
  compounds as impurities in clay, 428.
    in brick clays, 374.
    mineralogical nature of, 428.
  constitution of, 357.
  corrosive action of, 496.
  crystalline, 357.
  decolorising effect of, 102.
  effect of, on bauxite bricks, 499.
    on clay, 495.
    on earthenware body, 567.
    on electrical resistivity, 612.
    on expansion of glazes, 597.
    on firebricks, 149.
    on porosity, 66, 68.
    on strength, 147.
    on silica glass, 498.
    water on, 503.
  eutectics with felspar, 482.
  felspars, 367.
  firing temperature of, 558.
  formation of, 367.
  fusing-point of, 467, 600.
  glazes, 385.
  heat evolved in slaking, 529.
  heat of formation of, 531.
  in clays, 367.
    effect of, 368.
  in glazes, 387.
  in phase diagram, 475.
  in porcelain, 377.
  -iron oxide system, 471.
  kiln, effect of vapour-pressure in, 441.
  latent heat of fusion of, 600.

Lime *continued*—
-lithia-silica system, 476.
-magnesia-silica system, 474.
melting-point of, 605.
molecular heat of, 598.
olivine, 467.
production of, 434.
-silica system, 367, 467.
-soda-silica system, 476.
specific heat of, 598.
-strontia-silica system, 476.
Limestone, 367, 402.
calcining purpose of, 26.
Limestones, concretionary, 25.
crystalline, structure of, 14.
decomposition of, by heat, 433, 440, 545.
effect of carbonated water on, 504.
of percolating water on, 506.
occurrence of, 428.
oolitic, 25.
structure of, 7.
Limonite, 358, 359, 418.
a result of hydrolysis, 507.
as a cementing material, 15.
brown colour due to, 97.
colloidal, 419.
concretionary, 25.
decomposition of, by heat, 545.
magnetic properties of, 621.
melting-point of, 607.
water in, 423.
Linbarger, S. C., 184.
Lindstrom, R. L., 41.
Linear expansion, 521.
Liquid bubbles in crystals, 3.
to solid state, passage from, 487.
Liquids and gases, reactions between, 435.
effect of, on physico-chemical reactions, 445.
specific gravity of, determining, 226.
Litharge, effect of, on zirconia bricks, 500.
Lithia-barium oxide-silica system, 477.
-lime-silica system, 476.
-magnesia-silica system, 477.
-potash-silica system, 477.
-soda-silica system, 476.
-strontia-silica system, 478.
Lithium biotite, 417.
metasilicate, 326.
-potassium mica, 417.
silicate, 477.
Lithomarge, 20, 413.
structure of, 7.
Little, 477.
Loams, size of grains in, 34.
Lomas, J., 44.
London clay, 267, 273.
selenite in, 421.
grey stocks, crushing strength of, 173.
Loomis, G. A., 166, 566.
Losev, 236.
Loss of strength at high temperatures, 165.
on ignition, 362.
Lovejoy, C. H., 179.
Lowenstein, E., 337.
Lower Greensand, refractory sands in, 20.
Lowry's elutriator, 52, 53.
Ludwig, 526.
Ludwig's chart, 364, 382.
volumeter, 84.
Lundy, 219.
Lustre, 95.
Lustres, finishing temperatures for, 555.
Lutecite, 253.

M'Dowell, J. S., 14, 63, 79, 189, 218, 498, 499.
M'Gee, E., 188.
M'Leod, 616, 617, 618.
M'Mahon, 616, 617, 618.
Mackler, 391, 398.
Madagascar graphite, 23.
Magnesia, allotropic forms of, 355.
-alumina-silica system, 481.
system, 471.
amorphous, 356.
and fireclay bricks, interaction of, 498.
apparent density of, 219.
as a bond in silica bricks, 399.
as a flux, 486.
as an opacifier, 395.
bricks, 401.
and spalling, 584.
coefficient of expansion of, 581.
diffusivity of, 588.
effect of, burning temperature on, 591.
of carbides on, 498.
of carbon electrodes on, 499.
of carbon on, 498.
of conductivity of, 591.
of silica on, 498.
of steam on, 400, 499.
electrical resistivity of, 617.
Eubœan, crushing strength of, 187.
firing, 556.
temperature of, 558.
heat diffusivity of, 591.
hot, resistance of, to abrasion, 131.
strength of, 165.
under load, 179.
melting-point of, 605.
permeability of, 90.
porosity of, 79, 80.
practically insoluble, 503.
refractoriness of, 604.
resistance of, to abrasion, 130, 132.
to basic slag, 498.
to sudden changes in temperature, 583.

Magnesia bricks *continued*—
shrinkage of, 570.
spalling of, 583.
specific gravity of, 221, 588, 596.
heat of, 588, 596.
strength of, 160, 189.
Styrian, crushing strength of, 187.
texture of, 42, 43.
thermal conductivity of, 586, 588, 591, 592, 593.
effect of burning temperature on, 585.
thermal resistivity of, 594.
transverse length at high temperatures, 181.
calcined, properties of, 428.
thermal resistivity of, 594.
chemical constitution of, 355.
colloidal, 253.
crystalline, 356.
dead-burned, properties of, 428.
dead-burning, 556.
decolorising effect of, 102.
distinction of, from periclase, 625.
effect of iron oxide on, 498.
effect of, on electrical resistance, 612.
on porosity, 66, 68.
on terra-cotta, 148.
on vitrification range, 553.
water on, 503.
fused, hardness of, 132.
thermal conductivity of, 592.
fusing-point of, 467, 600.
heat of formation of, 531.
in glazes, 387.
in phase diagrams, 475.
in porcelain, 377.
-iron-oxide-silica system, 478.
system, 474.
latent heat of fusion of, 600.
-lime-silica system, 474.
-lithia-silica system, 477.
melting-point of, 605.
molecular heat of, 598.
polymerisation of, 356.
reaction of, with iron oxide, 474.
-silica system, 468.
-soda-silica system, 476.
specific gravity of, 219.
heat of, 598.
thermal conductivity of, 586, 592.
Magnesian limestone, 402, 428.
Magnesic porcelains, 378.
coefficient of expansion of, 576.
refractory materials, true specific gravity of, 220.
Magnesio-ferrite, 474.
Magnesite, 401.
action of hydrochloric acid on, 503.
amorphous, structure of, 8.
Magnesite *continued*—
bricks, see Magnesia bricks.
calcining, purpose of, 26.
colour of, 97, 120.
crypto-crystalline, nodular, 25.
structure of, 8, 19.
crystalline form of, 4.
effect of heat on specific gravity of, 220.
of iron oxide on, 401.
on colour of, 120.
of silica in, 401.
on refractoriness, 368.
fluxing oxides in, 401.
hardness of 126.
impurities in, 427.
in clay, 421.
occurrence of, 427.
segregation of, 25.
spar, 427.
texture of, 43.
true specific gravity of, 220.
structure of, 14, 21.
texture of, 42.
true specific gravity of, 211.
Magnesium aluminates, hydraulic properties of, 503.
carbonate as a cementing material, 15.
decomposition of, 490.
heat of formation of, 531.
chloride, heat of formation of, 530.
compounds, 368.
mineralogical composition of, 427.
effect of, on silica glass, 498.
metasilicate, 333.
melting-point of, 607.
mica, 417.
minerals in clays, 421.
orthosilicate, melting-point of, 607.
silicates, hydraulic properties of, 503.
fusing-point of, 467, 468.
spinel, 400.
graphic formula of, 356.
Magnetic hæmatite, electrical conductivity of, 609.
oxide of iron, colours produced by, 103.
formation of, 531.
in clay, 366.
in raw materials, 97.
See also Magnetite.
properties of ceramic materials, 608, 621.
of minerals, determining, 621.
separation, use of, 409.
Magnetite, 303, 357, 418.
crystalline form of, 4.
electrical conductivity of, 609.
formation of, 440.
hardness of, 126.
in silica bricks, 426.

Magnetite *continued*—
inversion of, 357.
magnetic properties of, 621.
melting-point of, 607.
replacement of, by hæmatite, 5.
space-lattice of, 324.
structure of, 7.
Mailey, 605.
Majolica ware, finishing temperature of, 555.
Major calorie, 509.
Making ceramic articles, 227.
Malachite green, use of, 251.
Malade jaune, 121.
Mallard, 216.
Malleability explained, 139, 142.
Malms, London, colour of, 114.
size of grains in, 34.
Manchester red bricks, strength of, 173.
Manganese compounds, colour produced by, 118.
in clays, 368.
discoloration produced by, 121.
effect of, on colour, 116, 117.
minerals in clays, 422.
oxide-silica system, 470.
in crystalline glazes, 397, 398.
silicates, melting-points of, 470.
Mansfield fireclay, specific gravity of, 213.
Marcasite, 359, 419.
effect of weather on, 507.
Marls, effect of heat on porosity of, 69.
hardness of, 125.
red, 109.
size of grains in, 34.
Staffordshire, texture of, 34.
Marquardt's porcelain, 375.
coefficient of expansion of, 576.
Marriotte-Gay Lussac Law, 533.
Martin, G., 326.
Mass action, 446.
and hydrolysis, 448.
law of, 449.
effect of, on reactions, 446.
flow, 274.
Masses, effect of time on, 439.
Massive structure, 21.
Matrix, glassy, 16.
non-glassy, 18.
Matte glazes, 396.
Matteness in glazes, cause of, 396.
Matter, forms of, 1.
Maw, 102.
Mayer, A., 248.
H. C., 133, 231.
Mayley, 614.
Mazzetti, 356.
Measurement of binding power, 282.
colour, 123.
Measurement of plasticity, 276.
viscosity, 291.
Mechanical analysis, 44, 49.
Medina quartzite, 219.
bricks, after-expansion of, 569.
specific gravity of, 219.
Meerschaum, 333.
Meissen porcelain, 375, 378.
coefficient of expansion of, 576.
Melilite, birefringence of, 626.
formation of, 440.
Mellor, J. W., 48, 57, 83, 85, 112, 121, 163, 165, 188, 192, 196, 220, 244, 247, 261, 263, 265, 270, 309, 330, 337, 339, 340, 342, 345, 348, 349, 350, 351, 356, 388, 394, 483, 496, 497, 498, 522, 550, 565, 569, 572, 580, 581, 583, 598.
Melting-point, 484, 523, 524.
determination of, 526.
effect of impurities on, 485, 526.
on specific gravity, 211.
pressure on, 485, 526.
prolonged heating on, 526.
quantity heated on, 525, 526.
rate of heating on, 526.
shrinkage on, 526.
size of particles on, 525.
factors influencing, 525.
Melting-points of ceramic materials, 605.
metals and alloys, 541.
Mene, C., 343.
Merwin, 330, 339, 471, 474, 481.
Metallic lustre, 95.
vapours, destruction of firebricks by, 495.
Metasilicate, 332.
Metasilicic acid, 333.
Metasomatic replacement, 506.
Meusser, 505.
Mho, thermal, 518.
Miall, S., 301.
Mica, 417.
as a cementing material, 15.
as an impurity in clays, 445.
crystalline form of, 4.
determination of, in clay, 410.
optical sign of, 629.
effect of fusion on specific gravity of, 211.
of heat on dielectric strength of, 614.
on refractoriness, 364.
on shrinkage, 567.
in china clay, 20.
in clay, 360.
-kaolin mixtures, 365.
Microcline, birefringence of, 626.
crystalline form of, 4.
effect of fusion of specific gravity of, 211.

Microcline *continued*—
formation of, 440.
formation of clay from, 354.
refractive index of, 623.
Micro-crystalline structure, 15.
Microliths, 3.
Microscopical examination of clay, 406.
structure of fired ceramic materials, 407.
Midland clays, burned, colour of, 110.
tile clays, effect of weather on, 255.
Millard, E. B., 512, 514.
Milner, H. B., 627, 630.
Mineral impurities in clays, 414–423.
Mineraliser, 489.
Mineralogical composition of alumina, 426.
of aluminous materials, 426.
of calcic materials, 428.
of carbon and carbon compounds, 430.
of ceramic materials, 406.
of chrome ores, 429.
of clays, 406, 411.
of lime materials, 428.
of magnesia materials, 427.
of silica, 423.
of siliceous materials, 423.
of titanic materials, 428.
of zirconium ores, 429.
Minerals, arrangement of, 411.
containing water, 423.
in burned clay, 415.
optical identification of, 622.
similar to clay, 413.
Minneman, 612.
Minor calorie, 509.
Miscibility of clays, 250.
Miscible liquids, phase diagram of, 457, 458, 459.
Mitscherlich, 334.
Mixed crystals, 324, 334, 335, 336, 456, 480, 487.
composition of, 489.
formulæ of, 335.
heat effect in production of, 599.
silicates, 334.
Mixing, effect of, on strength, 155.
methods of, 60.
Mixtures, 300.
preparing, 283.
Mobility, 290.
effect, of, on chemical action, 441.
increase in, 561.
of atoms, 437, 438.
of clay, 276.
Modulus of elasticity of glasses, 188.
glazes, 192.
rupture, 145.
and porosity of bricks, 182.
determination of, 197.
effect of firing temperature on, 162.
Modulus rupture *continued*—
of bricks, 176.
at high temperatures, 181.
of cold silica bricks, 187.
Mohs' scale of hardness, 124.
Moissan, H., 220.
Moisture, 362.
absorption of, 254.
distribution of, 254.
effect of, on apparent density, 206.
on strength, 166.
in clay, 370.
in raw materials, influence of, 256.
Molal latent heat, 524.
Molasses as a bond, 153.
Mole defined, 600.
Molecular attraction, effect of, on plasticity, 261.
compounds, 302, 341.
formulæ, 309.
and norms, 315.
calculation of, 312.
composition from, 311.
objections to, 314.
use of, 306.
heat, 513.
of alumina, 598.
of lime, 598.
of magnesia, 598.
of silica and silicates, 598.
of vaporisation, 524.
solution, 11.
structure of colloids, 322.
of solids, 322.
weight, 304.
Molecules, 300.
Moler, 7.
Molten mass, cooling of, 487.
masses, solidification of, 487.
material, solvent action of, 442.
mixture, changes in, on cooling, 457.
solidification of, 457.
Molybdic acid as catalyst, 443.
oxide in crystalline glazes, 397.
Monazite, action of hydrochloric acid on, 503.
crystalline form of, 4.
electrical conductivity of, 609.
hardness of, 126.
refractive index of, 623.
sands, 21.
Monosilicates, 332.
Montgomery, R. J., 186, 207, 220, 364, 478.
Monticellite, 474.
melting-point of, 607.
Montmorillonite, 20, 345, 413.
Moore, B., 112, 121, 249.
J. K., 67, 81, 84, 168, 196, 210, 211, 232, 492, 595.

Morscher, 608.
Mortar, effect of salts in, on scumming, 122.
Mortars for silica bricks, 498.
Moseley's law, 301.
Mottled clays, causes of colour of, 108.
colour, cause of, 111.
Mould, 122.
Moulded articles, effect of porosity on, 75.
Moulding, effect of size of grains on, 30.
of small grains on, 64.
processes, water required for, 270.
sands, porosity of, 75, 79.
texture of, 41.
Mucilage as a bond, 153.
Muffles, permeability of, 89.
porosity of, 78.
refractoriness of, 604.
texture of, 38.
thermal conductivity of, 588.
Multiple proportions, law of, 302.
Murray, H. D., 231.
Muscovite, 342, 417.
and alumina eutectic, 483.
birefringence of, 626.
decomposition of, by heat, 545.
electrical conductivity of, 609.
melting-range of, 607.
refractive index of, 623.
water in, 423.
Myelite, 413.
Mylius, 505.

Nacrite, 20, 412.
structure of, 7.
Naphthalene, use of, to increase porosity, 66.
Nascent action, 444.
Naterleuss, kieselguhr at, 119.
National Brick Manufacturers' Association, 128, 176, 200.
Physical Laboratory, 163, 616, 617.
Natrolite, 342, 345.
Navias, 329.
Nepheline, 416, 480.
action of hydrochloric acid on, 503.
bifringence of, 626.
formation of clay from, 354.
melting-point of, 607.
refractive index of, 623.
with silica and sodium silicate, 480.
Nephelite, see Nepheline.
Nephrite, melting-range of, 607.
Nesbitt, C. E., 130, 134, 169, 187, 206.
Neumann, 300.
Neutral salt defined, 321.
substances defined, 321.
Neutralisation an exothermal reaction, 520.
heat of, 530.
Neutrality or form of equilibrium, 435.
New Caledonia, chromite in, 430.
Newark, gypsum and selenite at, 428.
Newtonite, 345.
Nickel-chrome alloys, corrosive action of, on silica glass, 498.
compounds, colours produced by, 118.
effect of, on silica glass, 498.
oxide, effect of, on colour, 116, 117.
in crystalline glazes, 397, 398.
Nicol prisms, 627.
Nielson, O., 606.
Nitrates, a source of scum, 122.
Nitre, 122.
in glazes, 387.
Nitric acid, effect of, 504.
Nodular flint, 25.
structure, 25.
Nomenclature of acids, bases, and salts, 316–318.
of silicates, 332.
Nonpariel bricks, apparent density of, 219.
specific gravity of, 219.
thermal conductivity of, 586.
Non-plastic materials, casting, 285.
colours of, 118.
effect of, 270.
Nontronite, 367, 418, 419.
as a source of colour, 97.
decomposition of, 450.
water in, 423.
Normal salt, defined, 320.
Norms, 315, 483.
Northrup, 498.
Northumberland fireclays, barytes in, 15.
copper-iron sulphides in, 420.
North Wales ganister, texture of, 40.
red-burning clays of, 109.
Yorkshire, texture of ganister of, 40.
Notation, 306.
Nottinghamshire, red-burning clays of, 109.
Noyes, 229.
Nuclei of atoms, 301.

Ober, 235.
Obsidianite bricks, structure of, 18.
O'Connor, F. B., 129, 134, 199.
Odour of clays, 137.
Office, L. R., 186, 208.
Ogden, L., 144.
Ohm, thermal, 518.
Ohmic resistance, 608.
Oil as bond for carbides, 405.
absorbed by clay, 239.
clays, 370.
in clays, 276.
shale, origin of oil in, 422.

Oiliness of clays, 276.
Oils, mineral, as bonds, 153.
Oligoclase, 367, 417.
  birefringence of, 626.
  effect of fusion on specific heat of, 211.
  refractive index of, 623.
Olive-green colour, producing, 116.
Olivine, 416.
  action of hydrochloric acid on, 503.
  birefringence of, 626.
  crystallisation of, 461.
  electrical conductivity of, 609.
  formation of, 440.
  latent heat of fusion of, 601.
  magnetic properties, of, 621.
  melting-point of, 601.
    -range of, 607.
  refractive index of, 623.
Onyx, 424.
Oolitic limestone, 25.
Opacifying agents in glazes, 395.
Opacity, 631.
Opal, 253.
  as a cementing material, 15.
  modulus of elasticity of, 188.
  refractive index of, 623.
  specific heat of, 511.
  structure of, 7.
Opalescence, 94.
  in glazes, 392.
Opalescent glazes, 395.
Optical activity, 629.
  properties, changes in, due to heat, 532.
    of ceramic materials, 622.
  pyrometers, 536, 538.
  rotation of quartz, 425.
  sign, 628.
Optically active quartz, 629.
Ordinates, 455.
Ordway, 594.
Organic colloid matter in clay, 284.
  colouring matter in clays, 106.
  matter and plasticity, 264.
    souring, 275.
  colloidal, 253.
  effect of, on colloidal properties, 271.
  in clay, 284, 422.
Orthoclase, 342, 416.
  -albite-anorthite ternary phase, diagram of system, 463.
  birefringence of, 626.
  chemical formulæ for, 307.
  crystalline form of, 4.
    structure of, 2.
  effect of fusion of, on specific gravity, 211.
  graphic formulæ for, 309.
  isomorphism in, 334.
  melting-point of, 607.
Orthoclase *continued*—
  -quartz-plagioclase phase diagram, 464.
  refractive index of, 623.
  specific heat of, 597.
Orthosilicates, 332.
Orthosilicic acid, 333.
Orton, E., 98, 101, 102, 110, 128, 129, 260, 396.
Osann, B., 90.
Osceola insulating bricks, apparent density of, 219.
  specific gravity of, 219.
Osmosis, 230.
Osmotic pressure, 232.
Ostwald, Wo., 11, 231, 234, 249, 504, 509.
Ostwald viscosimeter, 293.
Ounces weight per pint of slips, 283.
Over-burning, 560.
  effects of, 442, 560.
  production of vesicular structure by, 610.
Overglaze decoration, 96.
Overheating, effect of, 442, 560.
Oxford clay, burned colour of, 110.
  coprolites in, 422.
  selenite in, 421.
Oxidation, 491, 507.
  a cause of colour, 107, 108.
  effect of, on clays, 256.
  objects of, 491.
  retardation of, 493.
Oxides, effect of, on coefficient of expansion of glazes, 579.
  iron ; see Iron oxides.
  nomenclature of, 320.
Oxidising atmosphere, colours produced in, 118.
Oxycarbides, constitution of, 357.
Oxygen ratio, in silicates, 332.
  strain, 385.

Paragonite, 417.
Parmlee, 392, 393, 633.
Parravano, 356.
Part, 627.
Particles, shape of, effect of, on reactions, 446.
Pascal, 606, 607.
Pastes, consistency of, 278.
  dry, nature of, 298.
  effect of acid on, 275.
  nature of, 1, 8.
  physical changes in, 257.
  preparing, 59, 283.
  refractory, 10.
  removal of water from, 295.
  retention of air by, 225.
  souring, 274.
  true specific gravity of, determination of, 225.
Patches in crystals, 3.

Paving bricks, 176.
apparent density of, 214.
finishing temperature for, 555.
hardness of, 129.
permeability of, 89.
resistance of, to traffic, 125.
Pearly lustre, 95.
Peaslee, W., 177.
Peeling and expansion, 578.
Penetrability, 86.
Penetration and durability, 502.
of slag into bricks, 501, 502.
Pennine, birefringence of, 626.
Pennsylvania, graphite in, 23.
Peptisation defined, 246.
Peptising agent, amount of, 288.
Perforated bricks, strength of, 150.
v. solid bricks, 150.
Periclase, 356, 428, 468.
crystalline form of, 4.
structure of, 14.
effect of size of grains on formation of, 43.
formation of, 438.
Peridotites, chromite in, 430.
Perimorphs, 3.
Period of weakness, 165.
Permanent volume-changes, 564.
Permeability, 86.
changes in, during burning, 547, 549.
smoking, 544.
determination of, 91.
effect of quartz on, 37.
of heat on, 88.
of, on drying, 89.
of, on thermal conductivity, 89.
of, on uses, 89.
shape of grains on, 28.
size of grains on, 30.
of pores on, 72.
of ceramic materials and articles, see under their respective names.
test, 91.
Perrin, 230, 232.
Perrot, 57.
Peters, 149.
Petit, 512.
Phakelite, chemical formulæ for, 307.
Phase conditions in ceramic processes, 466.
in chemical systems, 452.
diagram, 454.
of lime-alumina-silica system, 471, 477.
-ferric oxide system, 475.
-magnesia-silica system, 476.
of magnesia-alumina-silica system, 479.
-lime-silica system, 475.
of soda-alumina-silica system, 478.
Phase rule, 453.
Phases, solid, liquid, and gaseous, 452.
Phelps, S. M., 166, 495, 497, 498, 503.
Phenakite, 333.
Phillipon, M., 41, 64, 147, 151, 154, 219.
Phlogopite, 417.
electrical conductivity of, 609.
refractive index of, 623.
Pholerite, 20, 412.
Phosphate minerals in clays, 422.
Phosphates, action of hydrochloric acid on, 503.
as cementing materials, 15.
colour produced by, 112.
Phosphatic nodules, 422.
Phosphoric acid, combination of, with silica, 504.
as catalyst, 443.
effect of, 504.
Phosphorite, 422.
Phosphorus compounds in clay, 369.
Phyllite, 621.
Physical changes and chemical action, 433.
cause of, 433.
in cooling, 560.
form, effect of, on specific gravity, 208.
properties, effect of, on strength, 150.
state, changes in, effected by heat, 523.
effected by water, 227.
states of ceramic materials, 227.
structure, 1.
of clays, etc., 1.
Physico-chemical reactions between ceramic materials, 432.
Picolite, 427.
Pierson, 315, 413.
Piezo-electric effect, 611.
Pink discoloration, cause of, 121.
glazes, production of, 117, 395.
Pipes, porosity tests of, 83.
strength of, 177.
transverse strength of, determination of, 198.
Pirani, 614.
Plagioclase felspar, 417.
crystalline form of, 4.
formation of clay from, 354.
-quartz-orthoclase phase diagram, 464.
Plaster of Paris in glazes, 387.
Plastic bond, 153.
Plastic clays and colloidal substances, 228.
dried, strength of, 159.
organic matter in, 422.
porosity of, 75.
size of grains in, 35.
materials, 258.
cement in, 19.
Plasticity, 257–274.
actual *v.* potential, 277.
and best consistency, 267.
and binding power, 277, 281.
and carbonaceous matter, 370.

Plasticity *continued*—
and chemical composition, 259.
and colloid matter, 262, 277.
and compressibility, 280.
and deformability, 277.
and extensibility, 279.
and extension, 279.
and flow under pressure, 273.
and organic matter, 264.
and shear test, 281.
and viscosity, 273.
and water content, 277, 279.
effect of aggregation of particles on, 261.
of colloidal iron hydroxide on, 271.
of gum, etc., on, 275.
of intermolecular attraction on, 261.
of non-plastic materials on, 270.
of on flocculation, 246.
of pressure on, 270.
of sand on, 268.
of shape of particles on, 260.
of size of particles on, 260.
of soluble salts on, 241, 364.
of surface area on, 261.
increase and reduction of, 266.
increased by hydrolysis, 236.
increasing, 271.
measurement of, 276.
number, 268.
potential *v.* actual, 277.
proportion of water required, 267.
pseudo, 275.
range of, 268.
reducing, 272.
water of, 336.
required to develop, 262, 269.
v. cohesion, 9.
v. colloidal content, 9.
Platinum alloys, melting-point of, 541.
melting-point of, 541.
thermal resistivity of, 594.
Plauson mill, 13, 251.
Play of colours, 94.
Pleochroism, 95, 629.
Plumbago bricks, texture of, 43.
thermal resistivity of, 594.
crucibles, burning, 558.
for crucibles, 404.
occurrence of, 430.
thermal resistivity of, 594.
use of, 430.
Plumbiferous glazes, 388.
Pocket clays, 506.
structure of, 21.
Podszus, E., 251, 253.
Polarised light, 627.
for detecting structure, 3.
use of, 18, 406.
Polymerisation of alumina, 351.
of magnesia, 356.
Polymorphism, 325.
Polymorphous crystals, 5.
Popplewell, 173.
Porcelain, apparent density of, 214.
American, strength of, 178.
Bayeux, coefficient of expansion of, 577.
Berlin, coefficient of expansion of, 577.
beryllium, coefficient of expansion of, 574.
burning, 554.
casting, 284.
chemical composition of, 378.
chemical, strength of, 178.
Chinese, 376.
clays for, 375.
coefficient of expansion of, 577.
dielectric strength of, 613.
dure, 375.
effect of clay on coefficient of expansion of, 574.
of heat on dielectric strength of, 614.
electrical conductivity of, 609.
insulating power of, 612.
European, coefficient of expansion of, 575.
expansion of, 573.
firing, 559.
temperature of, 558.
fluxes in, 377.
glazes, 393.
hard, thermal conductivity of, 585.
Heinecke's, 378.
Hermodorfer, strength of, 178.
ideal, 375.
Japanese, 376.
magnesic, 378.
coefficient of expansion of, 576.
Marquardt, 375.
coefficient of expansion of, 576.
materials used for, 376.
Meissen, 375.
microscopical structure of, 488.
mixtures used for, 378.
piezo-electrical effect in, 611.
porosity of, 80.
puncture voltage of, 613, 615.
purpose of clay in, 377.
red discoloration in, 121.
refractoriness of, 603.
resistance of, to puncture, 610.
Seger, coefficient of expansion of, 576.
strength of, 178.
Sèvres, 375.
shrinkage of, 565.
sillimanite in, 17, 377.
specific gravity of, 214.
heat of, 596.
resistance of, 613.

Porcelain *continued*—
steatite, 378.
strength of, 177.
structure of, 17.
tendre, 375.
texture of, 40.
thermal conductivity of, 589.
resistivity of, 594.
translucency of, measuring, 634.
types of, 375.
Viennese, 375.
Pore-space, insulating properties of, 515.
Pores, effect of, on permeability, 88.
sealed, 204.
determination of, 83.
effect of heat on, 207.
formation of, 71.
proportion of, 205.
sealing, 546.
size of, 71.
effect of, on permeability, 72.
Porosity, 61.
and carbonaceous matter, 370.
and chemical action, 446.
and density, 205.
and modulus of rupture of bricks, 182.
and permeability of refractory bricks, 88.
and resistance to changes in temperature, 581.
to chemical action, 76.
and texture, 205.
apparent, determination of, 81; see also Apparent porosity.
changes and pressure, 567.
in, during burning, 547, 549.
smoking, 544.
vitrification, 552.
classification of ware by, 76.
coefficient, 62.
determination of, 81.
effect of vacuum on, 82.
determining, rough method of, 84.
effect of bonds on, 68.
of burning temperature on, 69, 70.
of Cornish stone on, 67.
of electrolytes on, 68.
of fineness of felspar on, 67.
of fluxes on, 67.
of fluxes on, 66, 68.
of grading on, 31, 64.
of heat on, 66, 69–71.
of, on absorption, 72.
on apparent density, 72.
on coefficient of expansion, 572.
on discoloration, 74.
on electrical conductivity, 74.
on moulded articles, 75.
on rate of drying, 75.
Porosity, effect of, *continued*—
on refractoriness, 74.
on resistance to abrasion, 73.
to corrosion, 73.
to erosion, 73.
to weathering, 73.
on scum, 75.
on spalling, 72.
on strength, 74, 152.
on thermal conductivity, 72, 514.
on uses, 75.
of pressure on, 62, 65.
of sawdust on, 72.
of shape of grains on, 28, 29.
of size of grains on, 30.
of texture on, 62, 63, 64.
increasing, 65.
low, testing, 80.
materials for increasing, 65, 66.
modes of expressing, 62.
of ceramic materials and articles, see under their various names.
reducing, 66.
true, 61.
determination of, 83.
Porous bricks, carbonaceous matter in, 65.
strength of, 182.
siliceous goods, density and specific gravity of, 219.
ware, 76.
Porphyry, 18.
electrical conductivity of, 609.
Portland cement as bond for carbides, 405.
in silica bricks, 399.
effect of, on firebricks, 495.
Pot clay, washed, apparent density of, 212.
Potash-alumina-silica system, 480.
effect of, on expansion of glazes, 579.
heat of formation of, 531.
in crystalline glazes, 398.
in glazes, 387.
in porcelain, 377.
-lithia-silica system, 477.
volatilisation of, 562.
Potassium carbonate, use of, in purifying clay, 288.
effect of, on silica glass, 498.
hydrate, effect of, on silica glass, 505.
metaborate, melting-point of, 607.
mica, 417.
Potters' flint, specific gravity of, 216.
Pottery clays, composition of, 372.
texture of, 37.
vitrification range of, 553.
water required to develop plasticity of, 269.
manufacture, china clay for, 372.
Potts, 214, 215, 574, 575, 578, 613.

Pouillet effect, 532.
Poulson, A., 252.
Powders, determination of permeability of, 93.
  mineralogical examination of, 407.
  porosity of, 75.
  thermal conductivity of, 592.
  true specific gravity, determination of, 224.
Precipitated silica, occurrence of, 424.
Precipitates, colloidal, nature of, 232.
Precipitation by electrolytes, 231.
  electrical, 230.
Preparation, effect of, on strength, 154.
  of homogeneous mixtures, 283.
Prepared cobalt, 395.
Pressure and chemical action, 440.
  critical, 485.
  effect of, on cementation, 507.
    on melting-point, 485, 526.
    on plasticity, 270.
    on squatting, 561.
Pressing, effect of, on strength, 157.
Pressure-equilibrium, 440.
  -flow and plasticity, 273.
  of fluidity, 126, 274.
  partial, of reacting constituents, 447.
Priest, 633.
Product, final, of reaction, 530.
Progress of reactions, 448.
Properties depending on structure, 27.
Proportion of elements in compounds, 302.
Proportions, equivalent, law of, 303.
  fixed, law of, 302.
  multiple, law of, 302.
Protection of colloids, 232.
  of clay suspensions, 249.
Protective colloids, 232.
Protons, 301.
Pseudo-acids and bases, effect of, on clay, 243.
Pseudo-plasticity, 275.
  -wollastonite, 467.
    specific heat of, 597.
Pseudomorphism, causes of, 5.
Pugging, 60.
  effect of, on strength, 155.
Pukall, W., 345, 347, 352, 368, 371, 376, 397.
Pukall's salt, 353.
Pulfrich, 443.
Pumice, 7.
  formation of clay from, 354.
  thermal resistivity of, 594.
Puncture voltage, 608.
  determination of, 620.
  of porcelain, 611, 613, 615.
Purdy, R. C., 56, 57, 81, 83, 84, 168, 211, 237, 243, 246, 248, 261, 262, 264, 266, 385, 387, 389, 392, 395, 397, 398, 483, 492, 574, 575, 576, 578, 613.
Pure clays, 414.
Purification of clay, 287.
Purple colour, cause of, 111.
Pycnometer, 225.
Pyrites, 359, 369, 419.
  a cause of discoloration, 121.
    of scum, 123.
  as a cementing material, 15.
  colour produced by, 103.
  cupiferous, discoloration produced by, 121.
  decomposition of, by heat, 545.
  effect of heat on, 366, 492.
  grey colour caused by, 97.
  production of spots by, 547.
  replacement of, by hæmatite, 5.
  scum due to, 419.
Pyrometer, Féry, 538.
  Le Chatelier, 538.
  Wanner, 538.
Pyrometers, electrical, 536, 537.
  optical, 536, 538.
  radiation, 536, 539.
Pyrometry, 509, 536.
Pyrophyllite, 345, 413.
  refractive index of, 623.
  thermal curve of, 352.
Pyroscopes, 536, 539.
Pyroxenes, 415.
  crystallisation of, 461.
  effect of heat on, 459.
  formation of, 440.
Pyrrhotite, 419.
  electrical conductivity of, 609.
  magnetic properties of, 621.

Quadrisilicates, 332.
Quantities, relative, effect of, 446.
Quarternary systems, 482.
  phase diagram of, 464.
Quartz, 328, 480.
  α-β-change in, 328.
  arrangement of atoms in, 327.
  as a cementing material, 15.
  birefringence of, 626.
  colour of, 119.
  conversion of, 329.
  crystalline, specific gravity of, 216.
    structure of, 2.
  determination of, in clay, 410.
  dextro- and lævo-rotatory, 629.
  effect of fusion of, on specific gravity, 211.
    of heat on, 329.
      dielectric strength of, 614.
    of repeated heating on, 218.
  electrical conductivity of, 609.
  formation of, 329.
  glass, 6, 487.
    coefficient of expansion of, 580.

Quartz glass *continued*—
effect of repeated heating on, 563.
permeability of, 89.
reaction of, with lime, 468.
ribbon-like crystallisation of, 327.
specific gravity of, 216.
heat of, 597.
strength of, 188; see also Silica glass.
hardness of, 126.
heat of solution of, 599.
in aluminium minerals, 427.
in china clay, 20.
in chromite, 430.
in magnesite, 428.
in zirconia ore, 429.
lustre of, 95.
made amorphous by grinding, 599.
melting-point of, 331, 605.
molecular heat of, 598.
occurrence of, 425.
optical activity of, 629.
rotation of, 425.
-orthoclase-plagioclase phase diagram, 464.
particles, signs of fusion of, 485.
piezo-electrical effect in, 611.
properties of, 425.
recognition of, in bricks, etc., 415.
refractive index of, 623.
replacement of, by hæmatite, 5.
rocks, structure of, 14.
separation of, from clay, 409.
solubility of, in hydrofluoric acid, 504.
specific gravity of, 217.
changes in, 217.
heat of, 510, 597.
thermal conductivity of, 592.
resistivity of, 594.
transformation of, 330.
unaltered, identifying, in silica bricks, 625.
volatilisation of, 561.
wedges, 628.
Quartzine, 253.
Quartzite bricks, 186, 400.
after-expansion of, 569.
Findlings, 17.
structure of, 18.
ideal structure of, 18.
Lickey, silicification of, 19.
Stiperstones, structure of, 19.
Quartzites, 425.
alteration of structure of, by grinding, 26.
calcining, purpose of, 26.
coefficient of expansion of, 579, 580.
colour of, 119.
composition of, 399.
crystalline structure of, 14.
specific gravity of, 216.
structure of, 14, 19.
Quartzites *continued*—
useful, structure of, 14.
useless, structure of, 14.
Queneau, A. L., 88, 92, 223, 585, 590, 592, 594.
Quensel, 443.

Race, 419.
Radcliffe, B. S., 389, 395, 610, 612.
Radiation, 519.
pyrometers, 536, 539.
Radicle, defined, 317.
Radiolaria, 7.
Rainwater, action of, on carbonates and silicates, 504.
Rakusin, 240.
Rammelsberg, 307.
Range of fusion, 486.
of plasticity, 268.
of vitrification, 552.
Rankin, 339, 471, 472, 473, 479, 481, 580.
Raoult, F. M., 525.
Rastall, 507.
Rate of chemical reaction, 446.
firing, 161.
Rational analysis, 409.
formulæ, 308.
Rattler test, 129, 199.
loss of weight in, 177.
Raw clays, see Clays.
Ray, R. C., 599.
Rayleigh, 327.
Reacting masses, distribution of, 451.
Reaction, existence of, 433.
heat of, 530, 599.
obscured, 531.
increasing velocity of, 450.
products, solubility of, 442.
Reactions accompanied by a change in temperature, 529.
arrest of, 550.
balanced, 451.
chemical, 435.
factors influencing, 437.
critical temperature of, 438.
due to acids, 503.
to alkalies, 503.
to water, 503.
effect of prolonged heating on, 562.
of temperature on, 435.
of time on, 439.
equilibrium, 452.
final product of, 530.
incomplete, 449.
involving displacement, 436.
irreversible, 450.
occurring at lower temperatures, 503.
at high temperatures, 490.

Reactions *continued*—
occurring in burning, 546.
in sand-lime bricks, 505.
of substances with each other, 432.
possible, 435.
progress of, 448.
reversible, 451.
simple, 452.
speed of, 449.
tendency of, 439.
thermo-chemical, 530.
velocity of, 449.
Rearrangement, chemical, 436.
Rebuffat, O., 218, 330.
Recalculated analysis, 410.
Rectorite, 345.
Recuperators, porosity of bricks for, 78.
Recrystallisation of rocks, 2.
Red bricks, apparent density of, 214.
finishing temperature for, 555.
importance of colour of, 547.
burning clays, 109.
cause of colour of, 109.
colour, effect of alumina on, 101.
of minerals on, 101.
of articles, cause of, 100.
colours, due to algæ, 97.
produced by iron compounds, 97.
production of, 97, 117.
discoloration, cause of, 121.
marls, 109.
Redlich, 339.
Reducing action, desirable, 493.
harmful, 493.
agents, 492.
atmosphere a cause of discoloration, 121.
colours produced in, 118.
Reduction, 492.
of iron compounds, 104.
processes and refractory materials, 493.
production of colour by, 111.
Reflection, 622.
Refraction, 622.
double, 625.
index of, 411, 622, 623.
Refractive index, 411, 622, 623.
determining, 624, 625.
indices of liquids, 624.
of minerals, determination of, 623.
Refractoriness and composition of clays, 381.
defined, 525.
determination of, 526.
effect of alkali on, 364.
of alumina and silica on, 364.
of felspar on, 364.
of heat on, 601.
of impurities on, 362.
of iron compounds on, 366.
Refractoriness *continued*—
effect of lime on, 367.
of magnesite on, 368.
of porosity on, 74.
of soluble salts on, 364.
of ceramic materials and articles, see under their various names.
of mixtures, 601.
of powdered mixtures of bricks with slag, 495.
of slags, 496.
Refractory articles, effect of frost on, 73.
firing, 556.
porosity of, 77.
bricks, resistance of, to abrasion, 130.
specific heat of, 596.
structure of, 17; see also under their various names.
coefficient, 381.
indices, 381.
materials and reduction processes, 493.
causes of colour of, 106.
electrical conductivity of, 74.
importance of porosity in, 72.
resistance to corrosion, 500.
strength, when hot, 164.
thermal conductivity of, 586.
pastes, 10.
porcelain, 378.
thermal conductivity of, 589.
silica sands, 400.
Refrax, effect of rapid cooling on, 584.
Regenerators, porosity of bricks for, 77.
Regnault, 513.
Rehydration of clay, 237, 349.
Reinforcement in ware, 377.
Relative colloids, 278.
quantities of reacting substances, effect of, 446.
Removal of water, changes following the, 294.
Renegade, E., 131, 136.
Repeated cooling, effect of, 563.
heating, effect of, 563.
on specific gravity, 218.
on strength, 163.
Re-pressing, effect of, on strength, 157.
Residual expansion of silica bricks, 568, 569.
Resilience explained, 139.
Resin as bond for carbides, 405.
Resinous lustre, 95.
Resistance, contact, 518.
electrical, 608.
and temperature, 611.
at different temperatures, 614.
variation of, with felspar content, 610.
ohmic, 608.
pyrometers, 538.
to abrasion, importance of, 124.

Resistance *continued*—
to acids and finishing temperature, 558.
to indentation, measurement of, 124.
to spalling, 583, 584.
to sudden changes in temperature, 581.
effect of size of grains on, 30.
Resistivity, 515.
electrical, 608, 609.
and exposure to electric current, 611.
determination of, 620.
effect of calcium sulphate on, 619.
of carborundum bricks, 619.
of chromite bricks, 618.
of fireclay bricks, 612.
of magnesia bricks, 617.
of silica bricks, 616.
of zirconia bricks, 618.
thermal, 584, 593, 594.
Retort bricks, thermal conductivity of, 593.
resistivity of, 594.
carbon, thermal resistivity of, 594.
settings, porosity of bricks for, 78.
Retorts, 557.
casting, 284.
effect of frost on, 73.
firing temperature of, 558.
interaction of, with contents, 491.
jointed, thermal conductivity of, 593.
laminated, cause of, 23.
permeability of, 90.
porosity of, 78.
refractoriness of, 604.
resistance of, to abrasion, 125.
to sudden changes in temperature, 582.
size of grog for, 39.
strength of, 183, 188.
texture of, 39.
thermal conductivity of, 588, 589.
effect of burning temperature on, 585.
Reverberatory furnaces, porosity of bricks for 78.
Reversible colloids, 235.
expansion of ceramic materials and articles, see under their various names.
reactions, 450, 451.
volume-changes, 520, 570.
Reversibility, 235.
Rhodochrosite, space-lattice of, 324.
Rhodonite, 470.
melting-point of, 607.
Rhyolite, formation of clay from, 354.
Rice, B. A., 480.
Richard, 600.
Riddle, F. H., 177, 574, 610, 612.
Riddling test, 45.
Rieke, R., 140, 143, 192, 217, 268, 269, 337, 364, 366, 367, 368, 481, 483, 577, 578, 579, 607.
Ries, H., 20, 63, 102, 151.
Rigg, G., 479.
Riley, 373.
Ring compounds, 308.
of ware, 137.
of well-fired goods, 556.
R.O. defined, 307.
Robertson, 189.
Rock crystal, specific gravity of, 216.
quartz, structure of, 14.
salt, replacement of, by hæmatite, 5.
by quartz, 5.
Rocks, action of water on, 506, 507.
cementing of, 15.
Rohland, 76, 238, 240, 246, 250, 255, 262, 263, 269, 270, 272, 275, 277, 284.
Rolling-out limit, 268.
test, 278.
Roofing tiles, colour of, 110.
finishing temperature of, 553.
hardness of, 129.
permeability of, 89.
texture of clay for, 37.
Roozeboom, 488.
Roscoe, 424.
Rosenow, 264, 265, 279.
Rosenthal, E., 177, 578, 613.
laboratory porcelain, coefficient of expansion of, 576.
Rosler, 354.
Ross, D. W., 188, 331.
Rotation, dextro- and lævo-, 629.
Rotatory power of quartz, 425.
Roth, E., 633.
Rouleaux in china clay, 19, 411.
Rounded grains, 27.
Ruabon aluminous fireclay, specific gravity of, 213.
clay, colour of, 109.
Rubber, effect of, on plasticity, 275.
Rubbers, friability of, 142.
strength of, 173.
Ruff, O., 79, 120, 231, 605, 606, 607.
Rugby red bricks, strength of, 173.
Rum, Isle of, ultrabasic rocks in, 461.
Rupture, see Modulus of rupture.
electrical, of porcelain, 611.
Russell, 598.
Rutile, 429.
birefringence of, 626.
crystalline form of, 4.
electrical conductivity of, 609.
hardness of, 126.
in clay, 421.
in crystalline glazes, 398.
in glazes, 398.
refractive index of, 623.
space-lattice of, 324.

Saggers, burning, 161, 557.
carborundum, a cause of discoloration, 121.
constancy of volume of, 582.
effect of frost on, 73.
of repeated heating on, 563.
firing, 161, 577.
temperature, 558.
laminated, cause of, 23.
permeability of, 89.
porosity of, 78, 582.
refractoriness of, 604.
strength of, 184.
of increasing, 161.
texture of, 37.
thermal conductivity of, 588.
"Salt," 122.
Salt, corrosive action of, 496.
defined, 316, 320.
glaze, 352, 383, 391.
alumina : silica ratio in, 391.
-glazed articles, finishing temperature of, 553.
bricks, finishing temperature of, 555.
glazing, 468.
Salts, effect of absorption of, 75.
on clays, 243, 494.
on electrical resistance of clay slips, 620.
on osmotic pressure, 234.
nomenclature of, 321.
removal of, from clay, 241.
from solution by clay, 241.
Samples, preparation of, for microscopical examination, 407.
Sampling, 360.
Sand-bauxite bricks, shrinkage of, 570.
weakness of, 149.
Sand-blast for testing hardness, 128, 134.
resistance of certain bricks to, 129.
test, 134.
Sand bricks, strength of, 185.
-clay mixtures, dry, strength of, 171, 172.
coarse, definition of, 35.
collodial properties of, 252.
dust, definition of, 35.
size of grains in, 35.
effect of, on plasticity, 268.
fine, definition of, 35.
size of grains in, 35.
surface factor of, 56.
Fontainebleau, sand-calcites in, 15.
for furnace linings, 21, 42.
porosity of, 79.
for moulding, texture of, 41.
hardness of, 126.
-lime bricks, 17.
reactions occurring in, 505.
structure of, 17.
See also Lime-sand bricks.
Sand *continued*—
moulds, texture of, 41.
separation of, from clay, 343.
size of grains in, 35.
thermal conductivity of, 592.
resistivity of, 594.
use of, in clays, 374.
Sands, chromite, 20.
dolomite, 20.
incoherent, use of, 426.
monazite, 21.
origin of, 21.
refractory, 20, 400.
zircon, 20.
Sandstones, calcareous, bond in, 18.
calcining, purpose of, 26.
cement in, 18.
dolomitic, 25.
electrical conductivity of, 609.
greyness of, 430.
siliceous, structure of, 18.
Sanitary ware, 392.
glazes for, 392.
Sankey, J. H., and Son, 591.
São Paulo, zirconia ore in, 403.
Sargent, 219.
Satin spar, lustre of, 95.
Satoh, P., 350.
Saturated compounds defined, 305.
Saunders, 493, 605.
Sawdust, effect of, on porosity, 72.
in clay mixtures, 371.
use of, to increase porosity, 65.
Saxe, C. W., 159, 161.
Scapolite, 342.
birefringence of, 626.
formation of clay from, 354.
melting-range of, 607.
Scheelite, crystalline form of, 4.
Scheffler, W., 385, 392.
Schists, electrical conductivity of, 609.
structure of, 23.
Schloesing, T., 263.
elutriator, 52, 53.
Schlossberg, A., 252.
Schoeffer, 231.
Schoene's elutriator, 51.
Scholes, S. R., 353.
Schorlemmer, 424.
Schory, 286.
Schott, 397.
Schramm, E., 199.
Schroeder van der Kolk, 624.
Schrotterite, 345.
Schulz, 598.
Schurecht, 55, 68, 155, 261, 266, 269, 398, 471, 482.
Schwartz, 216.

Schwarz, 326, 504.
Schwerin, B., 252, 253, 608.
Scotch bastard ganisters, texture of, 40.
fireclays, aluminous, 421.
copper-iron sulphides in, 420.
Scott, A., 68, 210, 330, 474.
Scratching tests, 123, 135.
Screening tests, 45.
Scum, 24, 75, 242, 367, 369.
blue-green, caused by ferrous sulphate, 97.
brown, 123.
cause of, 122.
due to pyrites, 419.
grey, 123.
in brick clays, 374.
prevention, 97.
of, by reduction, 494.
white, 122.
yellowish, 123.
Sealed pores, 204.
determination of, 83.
formation of, 71.
proportion of, 205, 207.
Seaton clays, barytes in, 421.
Seaver, 330, 331.
Sectility, effect of heat on, 138.
of clays, etc., 137.
Sedimentation, 53.
tests, 53, 54.
Seeds, use of, to increase porosity, 66.
Seger, 35, 98, 101, 102, 121, 150, 269, 363, 364, 381, 382, 384, 386, 389, 393, 395, 409, 472, 527, 540, 541, 574, 575.
cones, 540.
composition of, 379.
temperatures corresponding to, 379.
porcelain, coefficient of expansion of, 576.
dielectric strength of, 614.
strength of, 178.
Seger's imitation of Oriental porcelain, 376.
volumeter, 84.
Segregated structures, 25.
Selch, E., 479.
Selective action, 442.
Selenite, 367, 421.
effect of weather on, 507.
water in, 423.
Semi-grog bricks, apparent density of, 214.
true specific gravity of, 214.
-permeability of clay, 250.
-porcelain, apparent density of, 214.
porosity of, 80.
-silica bricks, 400.
effect of heating on volume of, 564.
Sensible heat, 520, 523.
Sentinel pyrometers, 540.
Serpentine, 416.
action of hydrochloric acid on, 503.
Serpentine *continued*—
as a cementing medium, 15.
birefringence, of, 626.
in chromite, 430.
in magnetite, 427.
refractive index of, 623.
rocks, chromite in, 430.
Sesquisilicates, 332.
Settling of particles in water, 54.
Sèvres imitation of Oriental porcelain, 376.
porcelain, 375, 378.
Sewer bricks, 175.
American, strength of, 176.
porosity of, 76, 77.
Shale bricks, apparent density of, 214.
thermal conductivity of, 590.
true specific gravity of, 214.
Shales, 237, 370, 414.
colour of, 108.
dry, strength of, 171, 172.
effect of heat on apparent specific gravity of, 208.
nature of, 22.
size of grains in, 34.
vitrification range of, 553.
water required to develop plasticity in, 269.
Shaly structure, 22.
Shape, effect of, on squatting, 561.
on strength, 150.
loss of, and rapid heating, 440.
of grains, 27.
effect of grinding on, 29.
on drying, 296.
on permeability, 28.
on porosity, 28.
on texture, 27.
for furnace hearths, 29.
Shaping, effect of, on strength, 157.
Shattering due to changes of temperature, 581.
Shaw, J. B., 196.
Shear test and plasticity, 281.
Shearer, G., 349.
Sheffield ganister, texture of, 40.
Shells, 376.
Shepherd, 467, 472, 525.
Shiners, production of, 117.
Shivering, 385.
Shore scleroscope, 136.
Shrewsbury, Stiperstones quartzites at, 19.
Shrinkage, 520.
and carbonaceous matter, 370.
effect of fineness of grains on, 565.
of fluxes on, 567.
of fused matter in, 567.
on melting-point, 526.
on strength, 160.
in drying, 295.
in kiln, measurement of, 541.

Shrinkage *continued*—
measurement of, as heat recorder, 541.
of aluminous materials, 570.
of bauxite bricks, 569.
of carbon crucibles, 570.
of engobes, adjustment of, 390.
of glaze, increasing or reducing, 390, 391.
of refractory bricks, 570.
permanent, 565.
Shropshire fireclays, copper-iron sulphides in, 420.
red-burning clays in, 109.
Siderite, 420.
electrical conductivity of, 609.
magnetic properties of, 621.
replacement of, by quartz, 5.
space-lattice of, 324.
Siemans, 614.
Sienna, 413.
Sieurin, E., 149, 363, 364, 366.
Sieves, kinds of, 45.
precautions with, 45.
relation of apertures in, 48.
standard, 45, 46, 47.
Sieving, 408.
test, 45.
dry, 48.
Sigur insulating bricks, apparent density of, 219.
specific gravity of, 219.
Sil-o-cel insulating bricks, apparent density of, 219.
specific gravity of, 219.
Silber, P., 338.
Silfrax, 357, 404.
Silica, affinity of fluxes for, 315.
allotropic changes in, 328.
forms of, 327.
-alumina-barium oxide system, 481.
-alumina eutectic, 472.
-lime system, 478.
-magnesia system, 481.
mixtures, refractoriness of, 472.
-potash system, 480.
-alumina ratio in clays, 371.
in glazes, 386.
rings, 472.
amorphous, 328, 329.
conversion of, to cristobalite, 329.
specific gravity of, 219.
and lime, reaction of, 434.
as an impurity in clays, 363.
-barium oxide-lime system, 474.
-soda system, 477.
system, 469.
-base-base ternary systems, 474.
bricks, 162.
acid reaction of, 497.
Silica *continued*—
bricks, after-expansion of, 569.
American, strength of, 186.
and spalling, 584.
apparent density of, 218.
bond in, corrosion of, 498.
bonds for, 399.
Brinell hardness of, 128.
cements for, 498.
coefficient of expansion of, 579.
composition of, 398.
crushing strength of, 187.
cristobalite in, 16.
diffusivity of, 588.
effect of alumina on, 497.
of ashes on, 497.
of basic fluxes on, 497.
of bonds on porosity of, 68.
of exposure on, 167.
of firing temperature on strength of, 162.
of fluxes on, 498.
of heat on conductivity of, 591.
on diffusivity of, 591.
of iron oxide on, 497.
of lime on strength of, 147.
of slags on, 497.
of texture on strength of, 185.
of tridymite on, 16.
electrical conductivity of, 616.
resistivity of, 616.
expansion of, 568.
firing, 556.
temperature of, 558.
forms of silica in, 426.
grading, 41.
hardness of, 132.
hot, strength of, 165.
under load, 179.
increase of refractoriness in, 497.
influence of burning on thermal conductivity of, 590.
iron compounds in, 426.
melting range of, 605.
mortars for, 498.
permeability of, 88, 90.
porosity of, 63, 64, 78, 80.
resistance of, to abrasion, 130, 132.
specific gravity of, 210, 218, 219, 588.
effect of burning temperature on, 217.
specific heat of, 588, 596, 597.
strength of, 185, 186.
structure of, 16.
susceptibility of, to sudden changes of temperature, 582, 583.
texture of, 40, 41, 63.
thermal conductivity of, 588, 589, 590.
at various temperatures, 586.

Silica *continued*—
bricks, effect of burning temperature on, 585.
resistivity of, 594.
transverse strength of, at high temperatures, 181.
tridymite in, 16.
use of flint in, 40.
cement, 15.
porosity of, 79.
refractoriness of, 603.
chemical formulæ for, 307.
coefficient of expansion of, effect of heat on, 580.
colloidal, 252.
as a cementing material, 15.
inversion of, 13.
constitution of, 326.
crystalline, 328.
effect of common salt on, 468.
grain size on inversion of, 330.
on expansion of glazes, 579.
on magnesia bricks, 498.
on refractoriness of clay, 364.
phosphoric acid on, 504.
flour, effect of, 219.
forms of, 328.
in bricks, 16.
free, 363.
fused, coefficient of expansion of, 580.
hardness of, 132.
permeability of, 89.
fusing-point of, 467.
gel, 252.
absorptive power of, 252.
glass, 328, 400.
attack of, by lime, 498.
by metallic oxides, 498.
by metals, 498.
crystallisation of, 488.
dielectric strength of, 617.
effect of phosphoric acid on, 504.
electrical insulating properties of, 616.
formation of, 331.
optical properties of, 631.
ribbon-like crystallisation in, 327.
solubility of, 505.
in alkalies, 505.
in hydrofluoric acid, 504.
specific gravity of, 216, 220.
inductive capacity of, 617.
thermal conductivity of, 591.
graphic formulæ for, 308, 326, 327.
hardness of, 126.
heat of formation of, 531.
hydrated, effect of alkaline solutions on, 505.
in clays, 414.
in combination, 363.
Silica *continued*—
in graphite, 430.
in lime glazes, 388.
in phase diagram, 475.
in solution, 506.
-iron oxide-magnesia system, 478.
system, 470.
-lime-barium oxide system, 474.
-lithia system, 476.
-magnesia system, 474.
-soda system, 476.
-strontia system, 476.
system, 467.
-lithia-barium oxide system, 477.
-lime system, 476.
-magnesia system, 477.
-potash system, 477.
-soda system, 476.
-magnesia-lime system, 474.
-lithia system, 477.
-soda system, 476.
system, 468.
-manganese oxide system, 470.
materials, 400.
mineralogical composition of, 423.
mortar, refractoriness of, 603.
occurrence of, 424.
-potash-lithia system, 477.
precipitation of, in rocks, 506.
reaction of, with bases, 505.
reduction of, 493.
by metals, 498.
retorts, strength of, 188.
rocks, 425.
fused, specific gravity of, 216.
lime in, 399.
potash in, 399.
structure of, 21.
sand, melting range of, 605.
-sillimanite system, 473.
slightly soluble in water, 506.
-soda-alumina system, 480.
-barium oxide system, 477.
-lime system, 476.
-magnesia system, 476.
-strontia system, 477.
system, 468.
solubility of, 504.
specific gravity of various forms of, 216.
heat of various forms of, 511, 597.
-strontia-lime system, 476.
-lithia system, 478.
system, 469.
thermal conductivity of, 593.
triplets, 327.
true melting-point of, 525.
use of, in glazes, 385.
volatilisation of, 491, 498, 561.

Silica *continued*—
ware, 400.
with sillimanite, 480.
with sodium silicate, 480.
-zinc oxide-alumina system, 482.
-zinc oxide system, 470.
-zirconia system, 470.
Silicates, 303.
action of water in, 503.
alkaline, effect of acid on, 333.
as cementing materials, 15.
chemical constitution of, 325, 332.
effect of fusing, 336.
of phosphoric acid on, 504.
of pressure in formation of, 440.
electrical conductivity of, 609.
formation of, 466.
fusing-point of, 467.
heat of formation of, 599.
hydrated, 336.
as cementing materials, 15.
hydrolysis of, 507.
in chromite, 430.
clay, 367, 415.
latent heat of fusion of, 601.
mixed, 334.
mobility of, 441.
nomenclature of, 332.
oxygen ratio in, 332.
specific heat of, 597.
Siliceous materials, burned, minerals in, 426.
coefficient of expansion of, 579.
colour of, 119.
effect of temperature of firing on, 580.
mineralogical composition of, 423.
refractoriness of, 603.
specific gravity of, 215, 216.
heat of, 597.
texture of, 40.
sandstones, structure of, 18.
sinter, 20, 253.
structure of, 7.
Silicic acid, colloidal, 252.
constitution of, 332.
water absorbed by, 237.
Silicification of ganisters, 19.
of quartzites, 19.
Silicon carbides, constitution of, 357.
manufacture of, 493.
fluorides, volatilisation of, 504.
hydrate, graphic formula for, 308.
nitride in carboxides, 357.
Silit, 357, 404.
Silky lustre, 95.
Sillimanite, 333, 342, 413, 478, 480, 481.
-alumina eutectic, 473.
birefringence of, 626.
bricks, structure of, 17.
Sillimanite *continued*—
crystalline form of, 4.
structure of, 2, 14.
crystals in porcelain, 377.
effect of, on electrical resistance, 612.
electrical conductivity of, 609.
formation of, 350, 472.
of clay from, 354.
hardness of, 126.
in glass-pots, 17.
in porcelain, 17, 377.
melting-point of, 607.
refractive index of, 623.
-silica system, 472.
thermal curve of, 352.
with corundum, 480.
with silica, 480.
Siloxicon, 357, 404.
decomposition of, 491.
effect of hydrofluoric acid on, 504.
bricks, burning, 557.
true specific gravity of, 221.
Silsbee, F. B., 615.
Silt, definition of, 35.
Humber, colour of bricks from, 110.
separation of, from clay, 343.
size of grains in, 35.
surface factor of, 56.
Silundum, 357, 404, 431.
colour of, 119.
true specific gravity of, 221.
Silver alloys, melting-point of, 541.
melting-point of, 541.
thermal resistivity of, 594.
Simonis, M., 247, 277, 292, 364, 381.
Sinclair, 337.
Singer, F., 347, 389, 395, 578.
Single oxides, 480.
Singulosilicates, 332, 466.
Size of grains, 29.
determination of, 44–59.
effect of, on allotropic forms, 31.
on chemical action, 445.
on drying, 30.
on lamination, 31.
on melting-point, 525.
on moulding, 30.
on permeability, 30.
on plasticity, 260.
on porosity, 30.
on resistance to temperature changes, 30.
on strength, 30, 150.
on surface, 31.
on texture, 29, 30.
in china clay, 33.
in clays, 33.
in goods, see Texture.
in kaolin, 33.

Size of grains *continued*—
in raw materials, see Texture.
of iron compounds, effect of, on colour, 99.
of silica in clays, 363.
Size of pores and absorption, 71.
effect of, on permeability, 72.
Skin on bricks and tiles, 123.
etc., producing, 38.
Slag blotches in firebricks, 115.
depth of penetration of, 501, 502.
-like masses in bricks, 416, 420.
(zinc) penetrability of, 502.
test, 495, 500.
Slags, action of, on bricks, testing, 501.
and silica, refractoriness, of, 497.
basic, effect of, on bauxite bricks, 499.
calcic, 368.
corrosive action of, 441, 494.
effect of, 169.
of alumina on, 479.
on chromite bricks, 500.
on diaspore bricks, 499.
on magnesia bricks, 499.
on silica bricks, 497.
magnesic, 368.
refractoriness of, 496.
resistance of bauxite bricks to, 500.
of bricks to, 497.
of carborundum bricks to, 500.
of magnesia bricks to, 498.
of zirconia bricks to, 500.
rich in lime, 497.
Slaking of clay, 227, 257.
Slate, nature of, 22.
Slip clay, dried, strength of, 159.
Slips, 282.
casting, 10, 283.
clay for, nature of, 10.
consistency of, determination of, 226.
nature of, 1, 10.
preparation of, 60.
properties of, 290.
purification by means of, 287.
removal of water from, 294.
solid matter in a pint of, 226.
use of, 10.
viscosity of, 282.
volume-weight of, determination of, 226.
Slurries, 282; see also Slips.
Smithson, 341.
Smits, A., 325, 357.
Smoking, 544.
Soaking, 439.
effects of, 550.
prolonged, effects of, 562.
stage of firing, 550.
Society of Glass Technology, 78.
Soda-alumina-silica system, 480.
as a flux, 481.
-barium oxide-silica system, 477.
compounds in silica bricks, 399.
effect of, on clay, 247.
on crazing, 387.
on expansion of glazes, 579.
on strength, 155.
on zirconia bricks, 500, 506.
-felspar, 416.
heat of formation of, 531.
in crystalline glazes, 398.
in glazes, 387, 398.
in porcelain, 377.
-lime glass, corrosive action of, 496.
-lithia-silica system, 476.
-magnesia-silica system, 476.
-orthoclase, 417.
-silica system, 468.
-strontia-silica system, 477.
use of, in casting, 285.
in purifying clay, 288.
volatilisation of, 562.
with corundum, 480.
Sodalite, formation of clay from, 354.
refractive index of, 623.
Sodium carbonate, effect of, on alumino-silicates, 322.
on silica glass, 505.
on zirconia bricks, 500.
chloride as a corrosive agent, 494, 495.
effect of, on silica glass, 498.
hydrate, effect of, on silica glass, 505.
on strength of dried clays, 155.
on zirconia bricks, 500.
metaborate, melting-point of, 607.
metasilicate, 333, 468.
melting-point of, 607.
-mica, 417.
nitrate, space-lattice of, 324.
phosphate, effect of, on silica glass, 505.
silicate as a bond, 154, 405.
crystalline form of, 337.
effect of, on strength of dried clays, 155.
with nepheline and silica, 480.
with silica, 480.
spinel, 400.
sulphate, corrosive action of, 496.
tetrasilicate, 468.
tungstate as catalyst, 443.
Soft porcelain, 375.
wares, hardness of, 127.
Softening-point, 164.
determination of, 526.
factors affecting, 525.
prior to fusion, 524.
Soil as colouring agent, 111.

Sokoloff, A. M., 257, 350.
permeability apparatus, 91.
Solid and gas, reactions between, 435.
and liquid, reactions between, 435.
bricks, strength of, 150.
cooled, composition of, 487.
matter, weight of, in a pint of slip, 226.
solutions, 300, 336, 354, 382, 456, 460.
and eutectics, 459.
substances, nature of, 1.
v. perforated bricks, 150.
Solidification of molten masses, 487.
Solidifying point, 484.
Solids, reactions between, 435.
Sols, colloidal, 11, 12, 228; see also Colloidal sols.
Solubility, effect of, on reactions, 441.
of products of reaction, 442.
Soluble bases to be fritted, 387.
iron compounds, 367.
salts, 364.
a cause of scum, 122.
effect of, on clay, 242.
on plasticity, 364.
on refractoriness, 364.
in brick clays, 374.
in glaze, 387.
Solution and replacement by water, 506.
colloidal, 11.
heat of, 529, 599.
v. colloidal sols, 11.
Solutions, composition of, and the temperature of equilibrium, 600.
heats of reaction in, 530.
ionized, 530.
molecular, 11.
nature of, 11.
solid, 300.
Solvent, action of molten material on, 442.
Soot a cause of discoloration, 121.
Sortwell, 394, 397.
Sosman, R. B., 325, 327, 328, 329, 357, 367, 424, 469, 471, 472, 475, 486, 488, 562.
Souring, 274.
Space-lattice, 323.
types of, 323.
units, 323.
Spade mixing, 60.
Spalling due to lamination, 22.
to large grains, 16.
effect of grading on, 32.
of porosity on, 72.
of rapid cooling on, 584.
of magnesia bricks, 583.
resistance to, 523, 584.
Specific electrical resistance at different temperatures, 614.
Specific *continued*—
gravity, 203.
apparent, 203; see also Apparent specific gravity.
bottle, 225.
changes in, 204.
during burning, 548, 549.
determination of, 221.
effect of heat on, 207.
factors influencing, 207, 208.
of ceramic materials and articles, see under their various names.
true, 203, 205; see also True specific gravity.
heat, 510.
determination of, 512.
of ceramic materials, effect of heat on, 594.
variations of, with temperature, 595.
heats of various substances, 511.
inductive capacity, 609.
ohmic resistance, 608.
resistance of porcelain, 613.
volumes, 204.
Speckled bricks, 111.
Speed of reaction, 499.
Sphene, 429.
birefringence of, 626.
crystalline form of, 4.
in clay, 421.
pleochroism of, 630.
Spinel, 40, 471, 481.
crystalline form of, 4.
electrical conductivity of, 609.
formation of, 440.
hardness of, 126.
in clay, 421, 422.
melting-point of, 607.
refractive index of, 623.
Spinels, 400, 421.
constitution of, 356.
Splichal, J., 232, 243.
Spodumene, 342.
melting-point of, 607.
Spongy ware, 369.
Spots, black, in ware, 121.
due to pyrites, 547.
Spring, 440.
Sproat, I. E., 145, 288.
Spurrier, H., 121, 264, 275.
Squatting, 560.
effect of pressure on, 561.
Stability at various temperatures, 520.
of crystalline solids, 487.
of vitreous solids, 487.
Staffordshire blue bricks, cause of colour of, 103.
strength of, 173.

Staffordshire *continued*—
fireclays, copper-iron sulphides in, 420.
red marls, 109.
Staining liquids, use of, 407.
Stains, 507.
Staley, H. F., 178, 198, 201, 315.
Standard sieves, 45, 46, 47.
American, 45, 47.
British, 45, 46.
Stanger, 225.
Stansfield, 616.
Star silica bricks, 187.
after-expansion of, 569.
crushing strength of, 187.
Starch paste as a bond, 153.
Starke, H., 614.
State, change of, effect of, on reactions, 444.
States, physical, of ceramic materials, 227.
Staurolite, 416.
birefringence of, 626.
electrical conductivity of, 609.
magnetic properties of, 621.
refractive index of, 623.
Steam, action of, on magnesia bricks, 499, 503.
as a catalyst, 443.
corrosive action of, 495.
Steaming, 371.
clays, 256.
Steatite porcelain, 378.
Steel, thermal conductivity of, 587.
Steger, W., 192, 596, 633.
Stelzner, 482.
Stickiness, 267, 276.
Sticky clays, 267.
Stiperstones quartzite, structure of, 19.
Stirlingite, 482.
Stock bricks, strength of, 173.
Stoke's Law, 53.
limitations of, 54, 55.
triaxial diagram, 315.
Stoneware, 392.
clays, colour of, 108.
coefficient of expansion of, 576, 577.
electrical insulating power of, 612.
firing, 554.
glazes, 392.
permeability of, 90.
porosity of, 80.
vitrification of, 551.
Stony clays, size of grains in, 35.
Stormer, 281.
Stourbridge firebricks, specific heat of, 596.
fireclays, 254.
specific gravity of, 213.
Stratified masses, 22.
Streak, 94.
Streaks in crystals, 3.
of colour as decoration, 118.
Strength, 139.
and refractoriness, 166.
at high temperatures, 164.
measuring, 196.
at low temperatures, ratio of, to that at high temperatures, 165.
changes in, during burning, 547, 549.
during smoking, 545.
during vitrification, 552.
crushing, 144.
determination of, 193.
effect of ageing on, 156.
of blows on, 169.
of bond on, 153.
of burning on, 159.
of chemical composition on, 146.
of deposited carbon on, 169.
of drying on, 158.
of electrolytes on, 155.
of flue-dust on, 169.
of fluxes, 147.
of frost on, 167.
of grading on, 152.
of grinding on, 154.
of lime on, 147.
of method of mixing on, 155.
of preparation on, 154.
of shaping on, 157.
of physical properties on, 150.
of porosity on, 74, 152.
of pressure on, 157.
of repeated heating on, 163.
of repressing on, 157, 158.
of shape and size on, 150.
of grains on, 29.
of size of grains on, 30.
of slags on, 169.
of sudden changes of temperature on, 163.
of temperature during use on, 163.
of texture on, 150, 185.
of vitrified bond on, 160.
of weathering on, 166.
factors affecting, 146.
lack of, causes of, 161.
minimum allowed in Germany, 175.
for building bricks, 174.
of ceramic materials and articles, see under their various names.
tensile, see Tensile strength.
transverse, see Transverse strength; see also under the various kinds of strength.
Stringer, 280.
Strontia in porcelain, 377.
-lime-silica system, 476.
-lithia -silica system, 478.
-silica system, 469.
-soda-silica system, 477.
Strontianite, refractive index of, 623.

Strontium metasilicate, melting-point of, 607.
minerals, 421.
orthosilicate, melting-point of, 607.
silicate, 477, 478.
melting-point of, 469.
sulphate, 421.
Structural formulæ, 308.
Structure, alteration of, 25.
capillary, 24.
of clays, 76.
cellular, 23.
coarse, crystalline, 15.
concretionary, 25.
crypto-crystalline, 15.
crystalline, 14.
disadvantages of, 14.
value of, 14.
examination of, under microscope, 407.
fibrous, 25.
fine, crystalline, 15.
fissile, 22.
foliated, 23.
granular, 15.
types of, 14.
homogeneous, 21, 59.
ideal, of fired clay, 29.
laminated, 22.
massive, 21.
micro-crystalline, 5, 15.
nodular, 25.
of atoms, 301.
of ceramic materials and articles, see under their various names.
of crystals, 323.
physical, 1.
of clays, 1.
properties depending on, 27.
segregated, 25.
shaly, 22.
shown by the microscope, 15.
by polarised light, 18.
unstratified, 21.
Stull, 389, 395.
Sturm, 326.
Sublimation, 485.
pressure, 441.
Subsilicates, 332, 466.
Substances in chemical reactions, effect of, 448.
Sudden changes in temperature, effects of, 581.
Suffolk bricks, production of, 102.
white bricks, 112.
Sugar, effect of, in souring pottery mixtures, 275.
Sullivan, 612, 616, 617, 618, 619.
Sulphates a cause of scum, 122.
as cementing materials, 15.
decomposition of, by heat, 369, 491, 545.
Sulphates *continued*—
in clay, effect of, 241.
spoil slips, 285.
Sulphides, decomposition of, by heat, 492, 545.
effect of hydrochloric acid on, 503.
of nitric acid on, 504.
Sulphur, corrosive action of, 495.
dioxide, effect of, 493.
effect of, on porosity, 68.
in clay, 369.
Sulphuric acid, effect of, on aluminosilicates, 504.
on basic materials, 504.
on clay, 409, 504.
minerals soluble in, 409.
Sumach, effect of, on plasticity, 275.
Summering, 253.
Sunlight, effect of, on clays, 507.
Sunning, 253.
Supercooling, effects of, 466, 484.
Supersaturation, effects of, 484.
Surface area, effect of, on plasticity, 261.
clays a cause of scum, 122.
colour of, 108.
effect of heat on apparent specific gravity of, 208.
combustion, 238.
effect of size of grains on, 31.
factor, 56, 278.
flow, 274.
tension, effect of, on chemical reactions, 441.
of clay, changing, 247.
Suspensions, 282; see also Slips.
colloidal, 12.
Suspensoid, 12.
Sven Oden, 232, 243, 255, 264.
Swarte, 608.
Swedish silica bricks, specific gravity of, 219.
Swelling, 562.
of clay, 237.
Symbols, defined, 306.
Syneresis, 252.
Synthesis of clay, 352.
System, definition of, 453.
Systems, colloidal, 12

Tableware, glaze for, 393.
strength of, 178.
Talc as a cementing material, 15.
Talcspar, 427.
Tamman, 488, 489.
Tannic acid, effect of, on strength of dried clays, 155.
Tantalite, electrical conductivity of, 609.
hardness of, 126.
Tantalum pentoxide, melting-point of, 605.

Tap cinder, corrosive action of, 496.
penetrative power of, 497.
Tar as a bond, 153, 405.
Temperature, absolute scale of, 533.
advantages of slow rise in, 440.
and chemical activity, 322.
attained in the firing, effect of, on strength, 160.
Celsius scale of, 533.
Centigrade scale of, 533.
changes, effect of, on strength, 163.
of, 163, 519.
of, and strength, 163.
sudden, effect of, 581.
sudden, resistance to, 581.
-composition diagrams, 455, 456, 465.
critical, 485.
due to molecular movement, 509.
during use, 163.
effect of, on cementation, 507.
on ceramic materials, see under their various names.
on chemical reactions, 435, 437.
on crystallisation, 488.
on density, 205.
on diffusivity, 588.
on intensity of chemical action, 445.
on reaction, 438.
on specific gravity, 209, 588.
heat, 588.
on thermal conductivity, 588.
on vitreous solids, 487.
raising the temperature, 439.
Fahrenheit scale, 533.
finishing, of burning, 553.
measurement, 532.
of casting, 287.
of reaction, 438.
of ware and electrical resistivity, 611.
and insulating power, 611.
optimum, for souring, 275.
relation of, to heat, 508.
required to produce good colours, 110.
resistance of, to changes in, 581.
scales of, 509.
-time diagrams, use of, 465.
variation of specific heat with, 595.
working range of, 438.
Temperatures, high, reactions at, 490.
low, reactions at, 503.
Tempering, 60.
effect of, on silica bricks, 156.
on strength, 155.
Temporary bonds for carbides, 495.
Tensile strength, 140.
determination of, 193.
of clays, variations in, according to mode of drying, 159.
Tensile strength *continued*—
of glazes, 192.
Tension, surface, 441; see also Surface tension.
Tephroite, 470.
Ternary system, phase diagram of, 463.
in ceramics, 474.
Terra-cotta clay, felspar in, 417.
colouring, 100.
control of colour of, 110.
discoloration of, 121.
effect of frost on, 73.
of fluorspar on, 148.
of fluxes on, 148.
finishing temperature of, 553.
glazes, 386, 387, 392.
importance of colour of, 547.
minerals in, 415.
porosity of, 77.
strength of, 177.
texture of clay for, 37.
thermal conductivity of, 593.
resistivity of, 594.
Terrome, 231.
Tests, see under the various kinds.
Tetmaier, 150.
"Te" value, 609.
effect of beryllia on, 613.
Texture, 27.
and carbonaceous matter, 370.
and porosity, 205.
coarse, 27, 36.
objections to, 37.
producing, 36.
determination of, 44–59.
effect of, 151.
grading on, 31.
on abrasion, 38.
on coefficient of expansion, 576.
on corrosion, 38.
on durability, 38.
on porosity, 64.
on strength, 185.
on thermal conductivity, 514.
shape of grains on, 27.
size of grains on, 29.
fine, 27, 35.
objections to, 35.
producing, 33.
homogeneous, 59.
medium, 36.
producing, 36.
of ceramic materials and articles, see under their various names.
relation of, to porosity, 63.
Textures, comparison of, 56.
Thermal capacity, 510.
condition of a body, 508.
conductivity, 514.

Thermal conductivity *continued*—
determination of, 515.
effect of heat on, 584, 585.
of temperature on, 586, 587, 588.
of permeability on, 89.
of porosity on, 72, 74.
factors influencing, 514.
formula for, 588.
of ceramic materials and articles, see under their various names.
units of, 515.
curve of clay, 349.
curves of alumino-silicates, 352.
equilibrium, 509.
mho, 518.
ohm, 518.
resistivity, 593.
value of a reaction and heats of formation, 531.
Thermo-chemical reactions, 530.
-couple pyrometers, 536, 537.
Thermometers, 536.
gas, 536.
Thermometry, 509, 536.
Thermoscopes, 540.
Thickness of sample, effect of, on translucency, 633.
Thomas, S. G., 401, 402.
Thompson, H. V., 353.
Sir J. J., 301, 305.
Thoria, melting-point of, 605.
source of, 21.
Thorpe, T. E., 388.
Thugutt, 307, 338.
Tiles, apparent density of, 214.
black, 111.
blue, 111.
coefficient of expansion of, 573.
control of colour of, 110.
fireclay, transverse strength of, 182.
floor, resistance of, to traffic, 125.
hardness of, 129.
importance of colour of, 547.
porosity of, 77.
resistance of, to abrasion, 130.
roofing, permeability of, 89.
resistance of, to weathering, 166.
strength of, 177.
Time and mass, relationship of, 439.
effect of, on chemical reactions, 439.
of tempering, effect of, on strength, 156.
-temperature curves of ceramic materials, 464.
of fused substances, 489.
diagram, use of, 465.
Tin-bearing minerals in clays, 422.
oxide as opacifier, 395, 396.
Titaniferous magnetite, electrical conductivity of, 609.
Titanite, crystalline form of, 4.
electrical conductivity of, 609.
hardness of, 126.
melting range of, 607.
refractive index of, 623.
Titanium compounds, colours produced by, 118.
in clay, 368.
in zirconia ore, 429.
mineral nature of, 428.
materials, use of, 428.
in clays, 421.
orthosilicate, melting-point of, 607.
oxide, effect of, on alumina, 368.
on colour of zirconia, 120.
on porosity, 68.
on refractoriness, 368.
in crystalline glazes, 397.
in fireclays, 373.
in glazes, 397.
melting-point of, 605, 607.
Titanoferrite, magnetic properties of, 621.
Topaz, birefringence of, 626.
electrical conductivity of, 609.
formation of clay from, 354.
refractive index of, 623.
Torsion tests, 199.
Toughness explained, 139, 143, 281.
Tourmaline, 418.
as catalyst, 443.
birefringence of, 626.
electrical conductivity of, 609.
in china clay, 20.
effect of, 107.
melting range of, 607.
pleochroism of, 630.
refractive index of, 623.
Traffic, resistance to, 125.
Transition point of eutectic, 459.
Translucency, 632.
and finishing temperature, 376, 558.
measurement of, 633.
Transmission of heat, 514.
Transparency, 631.
Transverse or cross-breaking tests, 145, 197.
of bricks, 175.
at high temperatures, 181.
of clays, 170–172.
of pieces of sagger, 184.
Travers, M. W., 183.
Treading plastic materials, 59.
Tremolite, 416.
birefringence of, 626.
electrical conductivity of, 609.
structure of, 25.
Trials as pyroscopes, 541.
Triangular grading diagram, Feret's, 58.
Triaxial diagrams, 315.

Tricalcium aluminate, melting-point of, 606.
ferrate, melting-point of, 606.
silicate, 333.
Trichites, 3.
Trichroic minerals, 630.
Tridymite, 328, 426, 475, 480.
bricks, strength of, 188.
conversion of, into cristobalite, 331.
crystalline form of, 4.
structure of, 2, 14.
distinction of, from cristobalite, 625.
formation of, 329, 330, 443.
hardness of, 126.
in furnace hearths, 17.
in lime-silica system, 467.
in silica bricks, 16.
melting-point of, 331, 603.
produced from fused silica, 332.
refractive index of, 623.
of determination of, 625.
solubility of, in hydrofluoric acid, 504.
specific gravity of, 216.
Trimorphous crystals, 5.
Trins, 2.
Triple oxides, 480.
point in a system, 453.
Triplet, atomic, 327.
crystals, 2.
Trisilicates, 332.
Trisilicic acid, 333.
Troost, 578.
Trouton, 524.
True clay, 343.
determination of, 410.
porosity, 61.
determination of, 83.
specific gravity, 203, 205.
determination of, 224.
Truesite, 413.
Tschermak, 307, 309.
Tucker, 493.
Tufts in clays, 3.
Tungstic acids, as catalyst, 443.
oxide in crystalline glazes, 397.
Turgite, 419.
Turner, W. E. S., 70, 71, 135, 206, 207, 210, 213.
Twinned crystals, 2.
Two gases, reactions between, 435.
liquids, reactions between, 435.
Tyler, W. S., & Co., 45.

Ullmanite, space-lattice of, 324.
Ulrich, 597.
Ultrabasic rocks, chromite in, 430.
of Isle of Rum, crystallisation in, 461.
Ultramicroscopic particles, 630.
Umber, 413.
Under-burning, 560.
-cooled liquids, 354.
cooling, 487.
-glaze decoration, 96.
-heating, effect of, 407.
Unfired bodies, identified by colour, 106.
Unglazed ware, porosity of, 77.
U.S. Bureau of Standards, 45, 181, 182.
Unmixing, 283.
Unsaturated compounds, defined, 305.
Unstratified masses, 21.
Unwin, 173.
Uranium oxide in crystalline glazes, 397, 398.
Uses, effect of permeability on, 89.
of porosity on, 75.
Utility and composition of clays, 371.

Vacuum, effect of, in porosity determination, 82.
Valencies of principal elements, 305.
Valency, 305, 308.
Vale of Neath, Dinas sand in, 20.
Van Bemmelen, 235, 237, 264, 421.
Hise, 354.
Klooster, 469, 470, 607.
Van 't Hoff's Law, 461, 467.
Vanadium compounds, discoloration produced by, 121.
in clay, 369.
oxide a cause of discoloration, 123.
in crystalline glazes, 397.
in matte glazes, 396.
Vaporisation, latent heat of, 524.
molecular heat of, 524.
Vapour density and molecular weight, 305.
pressure, effect of, on chemical reaction, 440.
Vapours, destruction of firebricks by, 495.
Variation, definition of, 453.
Variegated colour, effects, 118.
Vein quartz, segregation of, 25.
structure of, 14.
Velocity constants of reactions, 449.
of a reaction, effects of heat on, 528.
of chemical reactions, 448, 449, 450.
of reaction, increasing, 450.
Venetian red, use of, 117.
Vermicules in china clay, 19, 411.
in clays, 3.
Vermiculites, 19, 411.
Vernadsky, 307, 309, 413.
Very porous firebricks, apparent density of, 214.
Vesicular structure, 610.
development of, 207.
Vicat needle, 199, 200, 280.
Viennese porcelain, 375, 378.
Violet colours, producing, 116.
Viscosimeters, 279, 291–293.

Viscosity and plasticity, 272, 273.
defined, 290.
effect of, on chemical action, 441.
on crystallisation, 488.
electrolytes on, 286.
measurement of, 290.
of colloidal sols, 234.
of slips, 282, 290.
increase of, 244.
Vitreosil, 400.
Vitreous lustre, 95.
solids, stability of, 487.
state, energy in, 487.
production of, 487.
substances, 6.
use of, in ceramic materials, 6.
Vitrification, 551.
and balanced reactions, 452.
and fluxes, 552.
effect of, on electrical conductivity, 74.
range, 486, 552.
of clays, 552.
rate of, 552.
Vitrified articles, effect of frost on, 73.
bonds, 154.
bricks, 175.
finishing temperature of, 553.
hardness of, 128.
resistance of, to abrasion, 128.
claywares, coefficient of expansion of, 573.
material, 484.
ware, production of, 463.
testing porosity of, 80.
Vivianite, 420.
Vogt, J. H. L., 440, 443, 461, 511, 600.
Voids, effect of grading on, 32.
Volatilisation, 551, 561.
of colour, 118.
silica, 491.
Volatilised substances, action of, 495.
Volume-changes due to heat, 520.
during burning, 547.
vitrification, 552.
permanent, due to heating, 564.
reversible, 570.
which occur during heating, 563.
critical, 485.
weight, 203, 222.
determination of, 221.
of bricks, 215.
of slips, 226.
Volumeter, Ludwig's, 83.
Seger's, 84.

Waage, 448.
Waele, A. de, 272, 279, 281, 290.
Wallace, 476, 477, 478, 480, 606.
Wall white, 24, 182.
Wanner, pyrometer, 538.
Ware, biscuit, colour of, 112.
glost, colour of, 112.
white, 112.
Wartenburg, H. v., 598.
Wartha, 309.
Washburn, E. W., 61, 85, 86, 329, 470, 600.
Washing test, 48, 49.
Washington, 315, 413.
Watanabe, 24.
Water, a source of scum, 122.
absorption of, by clays, 254.
absorbed by dry clay, 75.
acid, in silicates, 338.
action of, on rocks, 507.
and mobility of clay, 276.
and plasticity, 277, 279.
and rate of flow, 273.
carbonated, effect of, 504.
changes effected by, 227, 253.
colloidal, 336.
combined, in alumina, 340.
disintegrating effect of, 254.
effect of, on ceramic materials, 503.
on clay, 228.
on dolomite, 503.
on lime, 503.
on magnesia, 503.
on silicates, 503.
on strength, 154.
Water-glass, 468.
as a bond, 154, 399, 405.
use of, in purifying clay, 288.
heat of formation of, 531.
in clays, 423.
in minerals, 423.
of constitution, 336, 337, 358.
in clay, 371.
clay, evolution of, 350.
of crystallisation, 336, 337.
in clay, 371.
of hydration, 336, 337.
of plasticity, 336.
phase diagram of, 455.
proportion of, in slips, used for casting, 285, 286.
rate of flow of, in capillary tubes, 87.
removal of, by evaporation, 288.
during smoking, 544.
from pastes, 294.
from slips, 294.
required, effect of texture on, 30.
for different moulding processes, 270.
to develop plasticity, 262, 267.
Watkin, 152.
Watkin's pyroscopes, 540.
Watts, A. S., 165, 171, 275, 376, 481, 486, 575, 577, 610.

Weather, exposure to, 506.
Weathering, 227, 253.
  a cause of scum, 122.
  alteration of structure by, 26.
  artificial, 256.
  chemical actions in, 506.
  effect of, on pyrites, 419.
    on strength, 166, 167.
    porosity on, 73.
Weber, 287.
Wedge pyrometer, 538.
Wedging clay pastes, 59.
Wedgwood, 542.
Weight per pint of slips, 283.
Weimer, G., 613, 615.
Wein, 578.
Wenzel's Law, 484.
Wernicke, 14.
Western clays, burned, colour of, 110.
Wetting clay, rate of, 240.
Wetzel, G., 518, 588, 590, 592, 596, 598.
Wheeler, 260, 552.
Wherry, E. T., 334.
White, W. P., 597, 598.
  bricks, 112.
    strength of, 173.
  clay, 108.
  scum, 122.
Whiteware, 112.
  effect of iron oxide on, 366.
  finishing temperatures for, 553, 555.
Whitewash, 122.
Whiting, effect of, on firebricks, 495.
  on shrinkage of earthenware, 567.
Witherite as a cementing material, 15.
Whitmore, 395.
Whitney, 235.
Wholin, R., 339, 340.
Wilhelmy's Law, 449.
Willemite, 333, 397, 470, 482.
Williams, 392, 393.
Wilson, S. T., 595, 596.
Windsor firebricks, 373.
  loam, 373.
Wintering, 253.
Woestyn, 514.
Wolframite, crystalline form of, 4.
  electrical conductivity of, 609.
Wollastonite, 363, 415, 421.
  birefringence of, 626.
  forms of, 468.
  melting range of, 607.
  specific heat of, 597.
Wologdine, S., 92, 223, 515, 589, 590, 594.
Worcester, W. G., 77, 110.
Wright, 286, 468, 471, 473.
Wyoming, bentonite in, 412.
Xenotime, electrical conductivity of, 609.
  refractive index of, 623.
X-ray spectra, drawback to, 325.
  spectrum of china clay, 19.
    use of, 299, 307, 322, 324, 344, 349.
  structure of colloidal gels, 252.
X-rays and crystal structure, 322.
  structure shown by, 8.

Yaichiro Kitamura, 394.
Yates, W. H., 112.
Yellow colour in clays, cause of, 108.
    produced by iron compounds, 97.
    production of, 97, 117.
  discoloration of, 122.
  films, 507.
  -green stain, cause of, 123.
  goods, producing, 114.
  scum, 123.
  stains, 507.
Yellowstone Park, geyserite in, 424.
Yielding point, 164.
Yorkshire, red-burning clays of, 109.
Yttria, melting-point of, 605.
  source of, 21.

Zeolites as cementing materials, 15.
  in glazes, 355, 389.
Zinc-alumina-silica system, 482.
  -blende, space-lattice of, 324.
  corrosion of furnaces by, 495.
  metasilicates, 482.
    melting-point of, 607.
  orthosilicate, 482.
    melting-point of, 607.
  oxide as opacifier, 395.
    effect of, on colour, 116, 117.
      shrinkage, 567.
    in crystalline glazes, 397.
    in matte glazes, 396.
    in porcelain, 377.
    silica system, 470.
    use of, for increasing crystalline matter in glaze, 390.
  silicate in crystalline glazes, 397.
    in matte glazes, 396.
    melting-point of, 470.
  slag, penetration of, 502.
  spinel, 400, 482.
    graphic formula of, 356.
Zinnewaldite, 417.
Zircon, 333, 403.
  as catalyst, 443.
  birefringence of, 626.
  colour of, 120.
  crystalline form of, 4.

Zircon *continued*—
electrical conductivity of, 609.
fusing-point of, 470.
hardness of, 126.
melting-point of, 605.
occurrence of, 429.
refractive index of, 623.
sand, 20, 403.
space-lattice of, 324.
specific gravity of, 221.
Zirconia, 403.
articles, porosity of, 79.
as opacifier, 395.
bricks, 403.
and spalling, 584.
electrical resistance of, 618.
hardness of, 133.
hot, strength of, 165.
resistance of, to abrasion, 130.
to cement, 500.
to fluorspar, 500.
to oxides, 500.
to slags, 500.
to temperature changes, 583.
shrinkage of, 570.
strength of, 192.
Zirconia *continued*—
colour of, 120.
crucibles casting, 285.
porosity of, 79.
effect of titanium in, 120.
melting-point of, 470, 605.
occurrence of, 429.
polymerisation of, 358.
reduction of, 493.
-silica system, 470.
sources of, 20.
specific gravity of, 221.
heat of, 596, 598, 599.
structure of, 21.
water required to develop plasticity of, 269.
Zirconium compounds, mineralogical nature of, 429.
impurities in, 429.
silicate, melting-point of, 470.
Zirkel, 621.
Zoellner, 483.
Zoisite, 342, 418.
birefringence of, 626.
formation of clay from, 354.
Zschokke, 143, 195, 262, 279.
Zsigmondy, 232, 235.

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